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EDITORIALS

Tariff without Protection

CONGRESS has just passed a tariff bill which makes the success of the chemical industry quite impossible. This action has been taken in spite of its avowed willingness to support our industry. The production of many synthetic organic chemicals in this country has been rendered as difficult as was the making of bricks without straw in the days of Pharaoh. The chemical industry has been left to the mercies of the "I. G." Potash developments are simply wiped out.

The first effect of the Tariff Act will be the possible failure, in increasing numbers, of the smaller concerns devoted to the production of greatly desired specialties. The total capitalization of 45 of them is about \$30,000,000. The strongest of these concerns may be able to live long enough to develop new lines of production that will save something from the crash. Others may perhaps be taken into combinations, thus tending toward the very monopolies which we seek to avoid in America.

Another effect will be the discouragement of research and discovery. We wonder how many research organizations, perhaps on the verge of discoveries important to the human race, will disband in disgust and disappointment. Talent will be diverted from problems affecting public health and national defense, and the final results cannot but be seriously detrimental to the American people and to the economic future of America.

Allied lines will be adversely affected. Most of the money invested in these chemical plants has been paid for equipment. Producers of such raw materials as lime, salt, alcohol, sulfur, iron, and copper will all feel the effects.

The Tariff Act fails in that no consideration has been taken of present conditions abroad. The selective embargo for a short period would have enabled our industries to gain strength. With the return of normal conditions abroad they would have been in position to meet competition with very moderate tariff protection. This has all been lost in the present tariff. In its stead we have some products over-protected, some fully protected, but the great majority virtually unprotected. A chemical selling at fifteen cents carries a duty of sixteen cents, while articles selling for more than a dollar are less and less adequately protected, since they are subject to the same duty of sixty per cent ad valorem and seven cents a pound specific. This means that a great group of specialties cannot be produced in America.

Who is responsible for this condition of affairs? It is unfortunate that the chemical industry had to be in any way involved in politics. The chemical industry became something upon which to make political trades, and in the last hours of Congress the House and Senate engaged in the favorite government game of buck-passing. Those immediately responsible appear to be Senators Smoot, Moses, King, and LaFollette. It is hard to understand how Senator Smoot could battle, on the one hand for a high rate on sugar, when the interests he represents cannot hope to produce more than a fraction of the country's requirements, and yet work persistently from the start against an industry capable of producing eventually one hundred per cent of our country's needs. Senator Smoot is a powerful factor in Congress and from the start has fought the chemical industry. Why?

We are familiar with the tactics of Senator Moses and have our own opinions as to his motives. Senator King has been willing to carry out orders in the maneuvers and with Senator Moses threatened to filibuster against the whole

bill if efforts were made to save the chemical industry. Senator LaFollette, besides supporting Senator Smoot in the Finance Committee, has been in reserve when needed.

Among the men who gave time and intelligent thought to the problem are Frelinghuysen, Wadsworth, McCumber, Watson, Sterling, McLean, McKinley, Townsend, Ransdell, Bursum, Broussard, Lenroot, and Curtis.

At the request of the Secretary of the Treasury a final effort was made to extend the embargo for at least ninety days, to enable customs officials to prepare for the administration of the Tariff Act. The Ways and Means Committee of the House reported favorably a resolution to this end, but the House refused to take it up until assured of favorable action by the Senate. On a point of order that such legislation must originate in the House, the Senate Finance Committee voted seven to five against reporting Senator Wadsworth's resolution, although some felt that the favorable action on the part of the House Committee satisfied the parliamentary point. With both houses of Congress reported willing to take the suggested action, the matter died on a parliamentary point urged by Senator Smoot.

Verily Congress chasteneth those whom it loveth!

The chemical industry fared much better at the hands of the Democratic party, and yet several Democratic senators, who had signified their intention to vote for the embargo, voted against it upon being urged by the Democratic leader, Senator Simmons, to do so because it had become Republican legislation. The Republican party was restored to power largely because of dissatisfaction with economic conditions. Many of the "best minds" in the Government, men who are supposed to bring their talents to bear on pressing economic and business conditions, have been silent and inactive. Of all government departments, the War Department alone has stood by the chemical industry and has shown some comprehension of what it means.

What can we expect in the affairs of state under such methods of government as now obtain?

We have learned that the one way to deal with politicians is at the polls. At the present time the whole country is interested in politics and the coming election. We chemists should make it our business to learn at once what those who hope to represent us think about the chemical industry and what they propose. Generalities will not suffice. We believe there are ways of interesting any individual in what chemistry means to him personally, and unfortunately in most cases the appeal will have to be to his personal interests. If we could elect a more aggressively sympathetic Congress as a result of the present situation, the price the chemical industry is asked to pay might not be too high.

While we fight at the polls with one hand, we must do the best we can with the other to carry on the chemical industry under the conditions imposed. We must show our good faith by creating our own standards of excellence. We must win the support of Americans for our products through unsurpassed quality and fair dealing. Even with greatly thinned industrial ranks we go forward, confident that a Congress can be elected which, profiting by the errors made during the session just closed, will do what is necessary to repair as much as possible of the damage.

If the calamity which we fear for the chemical industry does not materialize, it will be a miracle of the first magnitude, due to superhuman efforts of American ingenuity in the face of overwhelming odds.

Added Incentive

FROM TIME to time announcements are made of special grants of funds for particular problems, but this is the first time a science in America has been able to point to a great annual prize to be awarded the chemist residing in America who is judged to have accomplished the most for his chosen science and the world's welfare. The letter announcing the gift is given in full in this issue of the *JOURNAL*, among the transactions of the Council at Pittsburgh (p. 886).

The prize is yet to be given a suitable name, but it will undoubtedly be indicated in the rules governing its award, which will shortly be worked out by a committee to be appointed by President Smith (in conference with representatives of the corporation that is the donor). We venture to hope that this prize may be called the Nichols Prize, so named in honor of our past president, W. H. Nichols, to whose interest in chemistry and to whose special efforts we owe the establishment of this prize.

Obviously, no human effort is expended without an incentive of some kind. A few men are content to work toward the achievement of an ideal with no other object in mind. Many seek the truth for its own sake, and the fame which goes with discovery is frequently sufficient to urge men to unusual mental and physical effort. Much too often work is performed for monetary rewards only, and under such circumstances becomes routine in character and more or less unsatisfactory in performance.

In doing the everyday work of the world, most people are paid as they go. It is when fundamental things are accomplished, quite beyond the appreciation of the average man who barter and trades, that we turn to unusual honors and rewards to pay in some measure our debt of gratitude. Only in rare instances have scientists been repaid through the commercialization of their work; yet the race profits most if they continue in their laboratories unswerving from their original purposes. Important discoveries are seldom appreciated at the time except by the group within which the genius labors. The world needs a greater output of work of this character, and so far-sighted men have offered various incentives to induce men first to prepare for such a career, later to be confirmed in their desire to pursue fundamental work in pure and applied science, and occasionally have offered great prizes for the rare and outstanding achievements.

At another time we shall present a list as complete as possible of the studentships and fellowships established as incentives to train for greater things. There are many such opportunities for men to demonstrate more than average ability and many thousands of dollars are invested annually for this purpose.

A \$25,000 prize for a chemist! Unrestricted as to the corner of chemistry in which he works, unlimited as to geographical location, free from the circumscriptions of time—just the ability and perseverance to do great things. Not only in 1923, but in each succeeding year this prize is to be awarded. We should like to see this prize won early in its history by some chemist who, although working more or less obscurely with meager equipment, in one of our smaller institutions, is nevertheless doing great things and serving as an inspiration to the man just entering industry.

What a splendid incentive has been added to those already existing for men to continue their attack upon chosen problems in the field of chemistry! What a great stimulation for American chemists to put forth the very best that is in them year after year! No one can prophesy the good that will come to the country and the race in future years because this prize has been established. An added incentive, it should inspire lofty visions of service through chemistry.

The Pittsburgh Meeting

THE PITTSBURGH Meeting was notable because of the large number of papers presented, the excellence of the program, the large attendance, and the successful management on the part of the local committees. We should fall far short of our duty if we did not express our gratitude to Acting-President Baker of the Carnegie Institute of Technology for placing at our disposal the dormitories and other buildings of his institution, and to Chancellor Bowen of the University of Pittsburgh for his cordial support.

The 453 papers presented before 17 divisions and sections speak eloquently for the productivity of American chemistry. Still, it brings forcibly before us a problem that has for a long time confronted us. The time has come when we must consider the desirability of establishing certain standards for meeting papers, and make it something of an honor to be allowed to present a paper. Such a standardization will tend to reduce the number of papers presented, thus affording more time for discussion. The importance of this action is emphasized by those of our number who have attended scientific meetings abroad, where—in marked contrast to American practice—learned discussion follows the presentation of practically every paper, adding immensely to its interest and value.

Too much cannot be said in praise of the Local Section for the splendid manner in which the entertainment features were conducted. The members were untiring in their efforts as hosts, and spared neither money nor time to contribute to our happiness and comfort. The industrial excursion on Friday was especially noteworthy.

Incidentally, chemists should take pride in the fact that a demonstration of the utility of chemical research illustrated with an internal combustion motor was permitted in Carnegie Hall, heretofore reserved for prima donnas and other artists.

We all came away from the Pittsburgh Meeting impressed with the fact that the chemical profession is looking up, and confident that the AMERICAN CHEMICAL SOCIETY is able to undertake and carry through whatever is worth while for chemists and chemistry.

Regulating Chemical Fire Hazards

CHEMISTS have often been accused of lacking proper interest in legislative matters, even when their own interests are vitally concerned. In no case has this been more forcibly illustrated than in the regulation of hazards incident to their own operations. A proper subject for municipal control, regulations along this line have been left largely in the hands of municipal fire departments throughout the country. In general, the guides by which such rules are drawn up have been little more than the personal experiences of the officials charged with this duty, aided in a general way by the rules of the Underwriters Laboratories. The result, as might be supposed, has been a miscellaneous collection of rules based on little more than an unwonted fear of anything of a chemical nature. In other words, a wholesale injustice has been done the industry without its having had a voice in the procedure.

A damaging fire in a warehouse situated in a thickly populated section of New York recently waked the fire prevention officials of the city to the dangers resulting from lack of logically framed laws. In conjunction with an association of warehousemen, the Bureau of Fire Prevention of the city has formed a committee to revise the regulations on the subject and welcomed the idea of having a representative of the

AMERICAN CHEMICAL SOCIETY sit with them in their deliberations. Following this suggestion, President Smith has appointed Dr. C. E. Munroe, chairman of the Explosives Committee, Division of Chemistry, National Research Council to represent the SOCIETY on this committee. Certainly no action more important to the industry as a whole could have been taken, and it is to be hoped that other municipalities will follow this admirable lead.

Recognition Won

THE FUTURE of the chemical industry is still somewhat uncertain, but we are optimistic as to the ultimate outcome, largely because of the recognition which has already been won for the science and the industry. There are, however, still too many men in public life who either fail to comprehend what chemistry means to America or who unhesitatingly put their personal interests before everything else. But a review of the discussions of chemical matters before both houses of Congress and congressional committees in the last few years cannot fail to convince us that our science has won recognition and that public men are beginning to acquaint themselves with creative, instructive, and productive chemistry.

The public press is finding in chemistry a subject of importance, both from the standpoint of news value and as a topic for editorial discussion. A notable example is an editorial on "Pandemic Chemistry" in the *New York Times* for September 11. After discussing certain features of the Pittsburgh Meeting, this editorial concludes:

Every boy and girl and in time every man and woman should through school, newspaper, book, and magazine have this knowledge. If our high school students were to approach the science in this way, they would have a larger view than if they tried to grasp the complex problems of atomic structure and to fill their minds with the names of elements; then, too, more of them might be inspired to study it. The great chemical exposition to be held this week in the Grand Central Palace gives the public an opportunity to get some comprehension of what the vast range of this science now is. Such knowledge should become "pandemic."

Much remains to be done to make a knowledge of chemistry pandemic. The recognition already gained encourages chemists to greater efforts, and when the public knows about chemistry its encouragement will be demanded and its place in our economic fabric made secure.

An Appreciation of Fundamentals

WE ALL know that it is the seeking for truth for its own sake that gives us data upon which our material progress depends. But this view is seldom expressed in the lay press. "Uncle Dudley" brought out the plain facts clearly in an editorial in the *Boston Globe* for August 4, 1922, in which he defended the 19th century under the caption "Spare Those Bricks." We quote several paragraphs:

We are prone to think of the 19th century as the one which gave us modern machinery; steam, electricity, flying and wireless. This machinery was a by-product of something far nobler, and would that it had been, or were now, so regarded. It was a by-product of a fine and disinterested search for scientific truth.

Scientific men disabused their minds of prejudice, religious bigotry, preconceived notions, narrow imaginings, and set forth to discover whatsoever of truth they could.

The harvest was tremendous. And out of it came discoveries of general scientific principles which made possible the invention of this modern machinery which has become so much a part of our daily lives. But had these men of science set out with no higher aim than the invention of such machinery, that machinery

never would have been invented. In order to do anything supremely well, one must be trying to do well the thing just next above it in difficulty and importance.

In the early days of the Darwinian movement, Huxley, its lecturer-prophet, saw how things were likely to go and pronounced a solemn warning. He perceived that converts were flocking to his banner for the sake of the loaves and fishes, and cried out that if mankind regarded science and its discoveries not as a lofty and well-nigh religious quest of truth, but only as a means of padding their daily existences with material and bodily comforts, then it were better that these discoveries be not made than that humanity should use them as upholstery to an ignoble sloth.

Huxley's worst fears appear to have been realized. The seizure of science to breed material wealth and heap up material comforts; the neglect of the fine spirit of truth-seeking, which alone gives science its fruitfulness, not to say its nobility, is exactly what happened. The 20th century was not 17 years old before every nation which had benefited by the discoveries of the 19th, was in a murderous struggle with and about the machinery of wealth-production; and science found itself conscripted to the task of human slaughter, which it performed with a thoroughness unexampled in history and which, if repeated, threatens to terminate history and civilization.

The 19th century has been blamed for sowing the seeds of the World War. As well blame your parents for your combative instinct.

We inherited two things from the 19th century. One was the example of a disinterested search for truth which made the Darwinian age an age of triumphs and secrets wrung from nature's close reserve. The other was the machinery which those discoveries made possible. The machinery, the material wealth, and the bodily comforts it has provided, we of the 20th century have grabbed, gobbled, used and abused. The results have been frightful beyond anything in recorded history. The lofty and dispassionate search for truth we have neglected. That was what made the 19th century great. It is the only thing that can make any century great. Until we apply it to the social quandaries created by this new machinery, our own century will have no greatness, nor anything but squalor.

Quackery to Walk Plank

FOR SOME years leaders in the American Medical Association have desired means for so educating the intelligent laity that quackery, from which we still suffer greatly, could find no fertile soil in which to flourish. The news service of the Association accomplished a great deal and yet was not just what was needed. Before the Great War it was decided to launch a journal to popularize medical information, but war work interfered.

Now that the printing plant is being greatly enlarged, the journal is to be undertaken under the initial guidance of Dr. V. C. Vaughan, who has been a leading spirit in the plan for years. People are to be told in an interesting way about public health, prevention of disease and curative medicine—all authoritatively. Misinformation will be shown up and we see dark days ahead for the quacks.

In chemistry we have also talked for years about a popular journal managed by our SOCIETY. The need and the opportunity still exist, and the difficulty is largely one of funds. The *Journal of the American Medical Association*, with a circulation nearing 100,000, earns a large sum annually and supports many worthy activities. With adequate support the publications of the AMERICAN CHEMICAL SOCIETY can also be developed into properties capable of earning a large part of the funds desired, not only for a popular journal of chemistry but for other worth-while projects. And we believe that to fill its mission properly a journal of popular chemistry must be managed by the AMERICAN CHEMICAL SOCIETY. Quacking wherever it exists must be made to walk the plank. Education is the best weapon and must be greatly extended. It is the education of our masses that constitutes our best defense against quackery, whether it be in economics, religion, science, or government.

PITTSBURGH MEETING AMERICAN CHEMICAL SOCIETY

The meeting was well attended—approximately 15,000 being present. The Pacific Coast, the Atlantic Coast, the Gulf Coast, and Canada, each sent a goodly number, which, when added to the number from intermediate points, constrained one to wonder at the persistent talk of hard times and railroad strikes. Evidently, expense accounts retain some of the flexibility of former days, and the seriousness of the railroad situation had been largely overcome except in the newspapers. The presence in the Mississippi delegation of the chemical family of Swan, consisting of a father and four sons, set a record for families of chemists. The delegation from the University of Washington was large enough to justify a meeting of its own, although the Pacific Coast delegation as a whole did not succeed in getting the meeting next fall for San Francisco. Milwaukee persuaded the Council to take the meeting there instead.

The General Meetings on Tuesday and the reception on Wednesday were all that could be desired. The excellent papers given at these meetings may be read on pages 887 to 905 of this issue. Our President's address, "Our Science," was enjoyed by the public as well as by the members of the SOCIETY.

Automobiles and the possibility of smoothing out the operation of the family flivver to compare with that of "high brow" cars by the judicious use of diethyl selenide or tetraethyl lead, received a just share of attention, following the paper and experiments by Midgley and Boyd at the General Meeting. While the authors admitted that great good might be accomplished in removing detonation knocks by their method, they were unwilling to admit that they had found a cure-all for automobile ills, and stated that the regular service stations would have to be called in almost as usual.

Then the smoker! The more said the better, for certainly it was a genuine success. "Section Q" must have rolled violently in its grave with jealousy that Syria Mosque should have housed an event so reminiscent. Several of the large industrial laboratories in the Pittsburgh district staged individual skits that were well calculated to arouse the envy of the vaudeville kings. The general title applied by the perpetrators was "H₂O," and there was nothing dry about it from the first entrance of Dr. Halogen, of Freshwater College, to the final exit of the beautiful Miss Oxy Gen, vivid vamp and sister to Hydro, the volatile virgin. Movies of the activities of the Pittsburgh Section, shown for the benefit of sectional chairmen and secretaries, included many valuable suggestions for keeping up interest. Then the chef of the mosque spread himself for the profound benefit of all. One of the most attractive features of the smoker was the program, which included songs (to popular airs) written especially for the occasion.

Wednesday and Thursday were profitably spent in divisional meetings and symposiums at the Carnegie Institute of Technology. Each Division was well attended and interest in the various papers ran high. The arrangements for caring for interdivisional visiting were well handled, including bulletins on the campus as well as in each divisional meeting room, which showed at all times the papers being read and those next expected.

The meeting of the Metric System Committee with representatives of twenty other scientific societies to consider ways and means of forwarding the general adoption of the

metric system in this country, was one of the features of Wednesday afternoon. The question of educating the general public to the advantages of the system was considered, and a resolution adopted to request the Bureau of Education in Washington to use such means as it might command to increase the more thorough teaching of the metric system in all schools. The meeting favored the double marking of goods with both the metric and avoirdupois quantities, as a means of gradually educating the public to the general use of the former. However, the general sense of the meeting was that the change from one to the other would best be accomplished by gradual educative means rather than by any radical step. Reports from the various organizations indicated that in every case except those of the civil engineers, architects, and electrical engineers, progress was being made in introducing the system into general use in the industry represented. The following organizations were represented at this meeting:

American Chemical Society, Eugene C. Bingham, *Chairman*
American Psychological Association, W. V. Bingham, *Secretary*
National Academy of Sciences, W. A. Noyes for T. C. Mendenhall
American Institute of Electrical Engineers, N. W. Storer for Charles E. Skinner
American Metric Association, W. W. Stevenson
Optical Society of America, Harry S. Hower
U. S. Bureau of Standards, F. S. Holbrook
American Statistical Association, Roswell H. Johnson
Geological Society of America, Roswell H. Johnson
American Electrochemical Society, R. E. Zimmerman
American Pharmaceutical Association, J. A. Koch
American Astronomical Society, Herman S. Davis
Maryland Academy of Sciences, Claude H. Hall
American Association of University Professors, A. Silverman for Carl D. Schwartzel
American Institute of Architects, T. E. Billquist
American Society of Civil Engineers, R. A. Cummings
American Medical Association, Paul N. Leech
Mathematical Association of America, Dr. Bishop
American Physiological Society, C. C. Guthrie
American Public Health Association, A. B. Wadsworth
Illuminating Engineering Society, E. J. Edwards

Friday's excursion to the plants of the Carnegie Steel Corporation and the American Window Glass Company was greatly appreciated by the more than 400 who attended. The smoothness attending all arrangements was certainly a credit to those in charge. The structural steel process was followed from the ore to the finished steel, and the immense by-product coking plant which furnished the fuel for the steel manufacture was inspected. Lunch was served by the Carnegie Steel Corporation in the giant air-compressor plant, and the party was taken on to the glass plant to inspect its complete cycle of operations from the raw material to the finished sheets. Saturday's excursions to various plants in the district were less well attended, but none the less interesting.

Beginning with the advent of the two woman councilors, Misses Pennington and Woodford of New York, the ladies were well represented at all the gatherings. Entertainment especially for the ladies consisted of theater parties, a drive to the Pittsburgh Field Club, an excursion to the factory of the H. J. Heinz Co., inspection of the library, museum, and art galleries of the Carnegie Institute, a lecture by Homer St. Gaudens, a most attractive garden party, buffet supper, and dance at Oak Manor (to which all were invited), a drive

to the Allegheny Country Club, and a farewell reception and musicale at the 20th Century Club.

The entire Pittsburgh Section, and especially those responsible for the various entertainments, provided a meeting which will be long remembered as one of the outstanding events in the history of the SOCIETY.

Council Meeting

The meeting, with an attendance of 120, began its work in excellent spirits, following the announcement by President Smith that a prize, as yet unnamed, but comparable to the Nobel prize in value and importance, has been provided for American chemistry. He read the following letter, which he had received from the Allied Chemical and Dye Corporation:

AUGUST 30, 1922

MY DEAR DR. SMITH:

Confirming our interview yesterday, it gives me great pleasure to state that the Allied Chemical and Dye Corporation desires to institute an annual prize of \$25,000 to reward the chemist, residing in the United States, who in the opinion of a properly constituted jury has contributed most to the benefit of the science and of the world. Realizing, as we do, the enormous influence which chemists working in all the fields of that science will have on the welfare of the world, we desire by this prize to so encourage the workers that even larger benefits should accrue than those which have already placed the world under such a debt of gratitude to the profession.

We desire that you shall make this announcement at such time and place as you shall deem best, and to take such steps as may be necessary to carry the matter into effect beginning with the year 1923. We assume that a committee, of which you will be chairman, will be appointed by you to consider and suggest the rules governing the selection each year of the chemist who is deemed most worthy.

We also assume that this committee will provide for the appointment of a jury to decide annually who should be the recipient. We would be glad if the committee would arrange the selection of this jury so that this Company would have the appointment of two members, it being understood that neither of those members should be connected with the Company.

We do not desire to limit the gift to any particular field of chemistry, recognizing as we do the importance of them all.

As the American Chemical Society is by far the largest organization of chemists, and represents every field of the science in its membership, we have thought it better to work through that Society, although not limiting the gift to its members. Our sole desire is to encourage chemists everywhere in our country to do even more than they have been doing for the general good.

We have not gone into details, as we value greatly the opinions of those who would naturally be asked to serve on the committee, and do not desire to trammel them in their deliberations.

Yours very truly,

(Signed) WM. H. NICHOLS, *Chairman*

The announcement was received with great applause and the President appointed a committee to prepare appropriate resolutions accepting the gift.

The by-laws of the Cellulose Division were accepted, and those of the Petroleum Section referred back to the Section, for discussion and presentation to the Advisory Committee at a later day. The by-laws as resubmitted were approved later in the week by the Advisory Committee.

Milwaukee was chosen for the autumn meeting of 1923, which will be held during the week beginning Monday, September 10.

The Secretary then made the important announcement that the Chemical Society (London), with which the Faraday Society will cooperate, has determined to join with the American Chemical Society in the management of the *Journal of Physical Chemistry*. Correspondence and details were presented and a motion to approve the action taken and the plan devised was unanimously adopted. A motion was passed in which the Council expressed the hope that the new Board of Editors will confer with the editors of the Journals

of the American Chemical Society, of the Chemical Society (London) and of the Faraday Society, in order to prevent unnecessary overlapping of the fields covered in their respective publications.

A. B. Lamb was reelected Editor of the *Journal of the American Chemical Society*, E. J. Crane of *Chemical Abstracts*, H. E. Howe of *The Journal of Industrial and Engineering Chemistry*, and W. A. Noyes of *Scientific Monographs*. The selection of associate editors for the *Journal of the American Chemical Society* and for *The Journal of Industrial and Engineering Chemistry* was left to the editors, their nominations to be approved by the Directors. John Johnston's report on *Technologic Monographs* was presented, followed by his resignation, effective December 31, 1922. The Council empowered the Advisory Committee to select his successor, and a vote of thanks was passed expressing appreciation for the admirable work which Dr. Johnston has done. Charles L. Parsons was unanimously elected Secretary of the SOCIETY, and an *ad interim* report of the Treasurer was presented showing that the SOCIETY, because of reduced costs and careful management, is keeping within its income.

The Advisory Committee was then empowered to select four members to represent the AMERICAN CHEMICAL SOCIETY on the Board of Editors of the *Journal of Physical Chemistry*, and suggestions were invited from members of the Council.

The motion to increase the allotments of Local Sections was again laid upon the table, to be considered anew at the Milwaukee meeting.

The Cornell Section presented an invitation to the SOCIETY to meet in Ithaca in 1924, which was filed for attention one year hence.

After discussion it was voted that no change be made in the policy toward student members, and that they should continue to receive the advantages of the \$10 rate so long as they are *bona fide* students majoring in chemistry in colleges and universities. The following motion was adopted with reference to the presentation of papers by nonmembers:

On recommendation of the Advisory Committee, it was voted that, owing to the large number of papers being offered by the AMERICAN CHEMICAL SOCIETY, it is a ruling of the Council that papers by nonmembers may be placed on the program only when of unusual importance, and then only with the joint approval of the Secretary of the Division and the Secretary of the SOCIETY.

A committee was appointed to consider the importation of scientific books at reasonable rates, and instructions adopted calling upon our Committee on Nomenclature to use its best efforts to bring about a more general use of approved chemical spelling and nomenclature by all concerned.

In discussing the various fellowships and studentships supported by industry, the Editor of *The Journal of Industrial and Engineering Chemistry* was instructed to do what he could toward securing a complete list for publication in THIS JOURNAL.

The following resolutions submitted by the Advisory Committee were unanimously adopted:

The AMERICAN CHEMICAL SOCIETY, representing every phase of pure and applied chemistry, in annual meeting desires to express its appreciation of those men in public life, who, notwithstanding the multitudinous demands upon their time, have been willing to endeavor to inform themselves regarding chemistry and its relations to public welfare, national defense, and industrial progress.

They are also to be commended for the manner in which they have declared their findings and the action which they have been willing to take toward securing results believed to be beneficial to our country.

The AMERICAN CHEMICAL SOCIETY further expresses its thanks to Francis P. Garvan, president of the Chemical Foundation, for his sincere efforts to secure for America a well-rounded chemical

industry, for his assistance in the education of the public to the importance of chemistry, and for his aid in fostering research and the publication of its results.

A. V. H. Mory gave a brief outline of the work of his committee on reorganization, indicated something of the scope which they intended to cover, answered certain questions with respect to the points under consideration, and expressed the hope that a constructive report might be presented at the New Haven meeting.

The concluding business of the meeting centered about the report of the Committee to consider the question of a non-society employment bureau, of which Charles L. Reese is chairman. The Committee recommended greater activity on the part of Local Sections and other groups in a position to aid men locally, and in assisting those employing chemists

to secure men well qualified for the particular place. This portion of the report was adopted, and followed by a motion calling for a consideration by the Committee after consultation with the Secretary of the SOCIETY and the Editor of *The Journal of Industrial and Engineering Chemistry*, of a plan to inaugurate in the office of the Secretary or the Editor of *The Journal of Industrial and Engineering Chemistry* a clearing-house for the exchange of information between Sections and other groups relative to any excess of either men or positions in various localities. A tentative budget based on this plan is to be presented at the Directors' meeting in December.

The Council adjourned with suitable motions expressing appreciation to all those who participated in making the Pittsburgh meeting so successful.

The Human Side of Chemistry

By Edwin E. Slosson

SCIENCE SERVICE, 1115 CONNECTICUT AVE., WASHINGTON, D. C.

A HUNDRED years ago chemistry was a toy. To-day it is a tool.

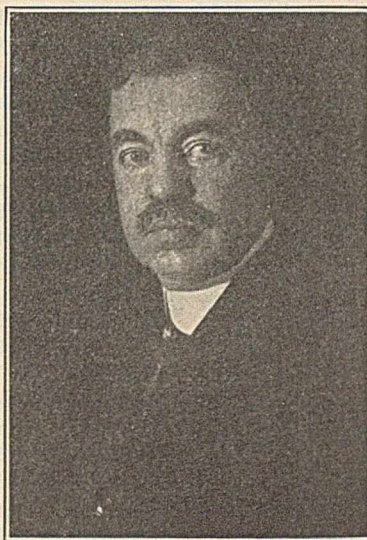
From the diversion of the philosopher it has developed into a practical profession of the highest importance to humanity. All the sciences may be expected likewise to earn their own living when they get old enough. But chemistry has in an astonishingly short time reached maturity and become more than self-supporting. We have recently seen factories hatching from test tubes, like fowls from eggs. Some of our friends in sciences that are older but do not yet pay dividends look upon chemistry with a certain suspicion and perhaps envy because of its success in a business way. They want to keep science as a sport and seem anxious lest the chemist lose his amateur status by making money. They need not worry, for whatever rewards come to the chemist—or to his employer—will be an infinitesimal fraction of what chemistry has given to the world.

THE CHEMIST TOO MODEST

The chemist is the most modest of men. He does not claim credit for what others do. He does not claim credit for all he does. Indeed, he often disclaims credit for some of his highest achievements. If he makes butter, he is willing that the credit should go to the cow, while he takes the cash; if he spins the silk for a dress he pretends that he is a mere worm; if he constructs a pearl he disguises himself as an oyster. He will even condescend to take the place of the humble tortoise and secrete a shell.

Modesty is an admirable thing, but it has its dangers if overdone. When you assume a deprecatory attitude toward your achievements, there is always the danger that other folks may believe you. They may take you at your own pricemark. It is safe to profess unworthiness only when you are sure that those present will contradict you.

The result of this persistent attempt of the chemist to minimize his own importance is that the outside world fails to ap-



E. E. SLOSSON

preciate the value of his contributions to modern civilization and does not at all realize what the chemist might do in the future if he had a free hand. Don't camouflage your creations by calling them imitations. If you invent a synthetic plastic, some condensation product of phenol with an aldehyde or an amine, don't call it a mineral or vegetable. Name it after yourself.

A synthetic product should have a synthetic name. One of the fortunate effects of the unfortunate failure of our patent laws to afford proper protection is that it has led to the coining of new names for new things; too often to the coining of new names for old things, it is true, but still a good movement, for it brings people to the recognition of the fact that there are new things under the sun and that most of them come from the chemist. The chemist has become the greatest coiner of words in the world. The rapid expansion of organic chemistry demanded the fabrication of some

250,000 new names, with provision for an indefinite increase in the future. Nobody ever had such a job since Adam was called upon to give names to all the animals as they filed before him. It meant doubling the dictionary. In accomplishing the gigantic task of constructive philology, the chemist has got some unwieldy combinations, but on the other hand he has under the pressure of commercialism contrived some very neat and handy nicknames for everyday use. The coinage of "Kodak" confounds the philologists. But they have determined the derivation of "balopticon" to their own satisfaction. It is derived, they say, from two Greek roots "ballo," to throw, and "optikos," sight, a very proper term for a projection lantern, and removes the suspicion that the name of the apparatus might conceal a sly reference to its makers, the Bausch & Lomb Optical Company.

This is much better than the old custom of carrying over old names to new things. Fish glue films were called isinglass as though they were a kind of glass. When mica took its place it too was called isinglass, even in stove windows, and what is now

called mica is mostly celluloid, and what is called celluloid, may be something else. Language lingers and lags behind the advance of science. That is because the public cannot realize the creative power of chemistry—that a compound is a different thing from the elements that compose it.

NEW ERA IN CHEMISTRY

In chemistry the whole is not equal to the sum of its parts, never qualitatively and possibly not always quantitatively. If we put together four atoms of hydrogen each weighing 1.008 we get one atom of helium that weighs only 4. The .008's have somehow got lost in the shuffle.

Chemistry is the creative science. Don't suspect me of taking advantage of my position to work in anything personal. I am quoting Berthelot, who foretold the time when all our foods would be made by the chemist. I do not see so far ahead as that, but it is certain that chemistry is entering upon a new era when its constructive powers will have wider scope and largely relieve us of our forms of life. The chemist of the future will not be content to do analytical work such as the housewrecker does, or imitative work such as the forger does, but the chemist will do original work such as he alone can do.

The future of civilization is fixed by the scientist because he has the power to control the basic reaction on which our vital and mechanical power depends, the oxidation of carbon and hydrogen. All wealth is in its essence energy, and the material sources of energy are practically but two, food and fuel, very similar in composition and just alike in their final products. If the fuel falls short, our modern civilization will disappear and humanity will revert to a primitive condition. If our food supply falls short, life itself will be limited. The two factors of civilization, mass and potential, population and the standard of living, quantity and quality, are functions of the food and fuel supply. The Law of Malthus has often been refuted but has never been repealed. The world has now been all surveyed and staked out in claims like a mining camp after the first rush is over. Quarrels over stakes and limits will continue and we can only hope that they will be settled in court rather than by the cruder methods of Roaring Camp. The late unpleasantness was started by a claim jumper who was too quick with his shooting iron and had to be handled by the vigilance committee. But how such quarrels are to be settled in the future is no more the concern of the chemist than of any other citizen. The peculiar business of the chemist is to see that there is something worth quarreling about. He is to show how to create and economize wealth and is not responsible for its abuse and destruction.

The period of the extension of civilization is approaching its end, and henceforth progress must take the form of intensification of civilization. People must cease to expand and begin to construct. There are no more continents to discover. No more worlds to conquer. The new era will require new methods and here the constructive powers of the chemist will come into play. The world will more and more come to depend upon him. It does not require any chemistry to pick a cocoanut off a palm tree. It only requires a rope and prehensile toes. But it does require chemistry to extract the oil from the copra and hydrogenate it and sell it as a bread spread to a hostile public. It does not require any chemistry to manure a field, but it does require chemistry to fix the free nitrogen of the air.

Chemistry is continually gaining ground from biology. Vast areas, which biologists once claimed but had neglected, have now gone over to the chemists. In fact, it seems that whenever a vital process or product had been thoroughly studied and understood, it is found to belong to physics or chemistry. Consequently, the chemist is inclined to regard biology as merely an unexplored province of chemistry. Many a loyal biologist in pursuit of some legitimate line of research well within his own territory has found in the course of time that he has unconsciously become a chemist. Pasteur many years ago crossed the

boundary in the opposite direction; while hunting up asymmetric crystals he got over into abiogenesis. As an offset to our gains from biology we have lost to physics the invaluable province lying inside the atom. In the *modus vivendi* that prevailed when I was a student, anything bigger than the molecule belonged to the physicist, and everything smaller to the chemist. But a band of bold physicists, led by Thomson and Rutherford, made a raid into the hinterland of chemistry and captured the interior of the atom. Scientific boundaries, like national boundaries, are merely imaginary lines and may be drawn at convenience, though they are mostly drawn at inconvenience.

The new era that we are entering is a period of merger in the sciences. The traditional boundaries are being wiped out. The nice precise little dogmatic definitions and distinctions that used to fill the first few pages of an elementary chemistry textbook have run together like bad dyes in warm water. The old arbitrary division lines between chemistry and physics, organic and inorganic, natural and artificial matter and energy, molecule and mass, chemical affinity and adhesive forces, are disappearing. Scientists are discovering what the artists have long known—that there are no lines in nature.

Acetic acid may be made by a vinegar plant *or* by a hydroelectric plant. A reaction may be accelerated by a high temperature *or* a catalytic metal. It has recently been announced that rickets in children may be cured by sunlight *or* cod-liver oil. Let us hope that the children will be allowed their choice of which remedy they will take.

Every annual session of this SOCIETY knocks some of our old ideas in the head. At this meeting Professor McKee will try to persuade us that there is no shale oil in oil shale, and Professor Bancroft that there is no color in the peacock's tail.

Chemistry is now passing through a revolutionary era like that of 150 years ago when Lavoisier's balance overthrew the phlogiston theory. But as Priestley stuck to phlogiston to the day of his death, although his discovery of oxygen had given it the deathblow, so some of us elders show a certain reluctance in relinquishing our old familiar images. There was something solid and satisfying about our molecular models made of wooden balls, stained with aniline dyes and stuck together with wires. But these have now been relegated to the top shelves of the storeroom and we have to get used to a newfangled atom, composed of a vacuum and algebraic symbols. Minus marks are flying round a plus mark like automobiles on a race course and whenever one skids it flashes its light. In place of a stout wirey valence bond, stiff and straight, that sticks when it is once put into its hole, we are offered two electrons playing tag in a ring, like cats chasing each other's tails.

But the new conceptions, as we all realize, are vastly in advance of the old, for they give us the ability to handle the ultimate and individual units of matter. Clerk Maxwell held that the laws of nature were merely and inevitably statistical, that we could only deal with averages of multitudes of indistinguishable molecules and movements. If that were true, chemistry would be less of an exact science than sociology, for the chemist cannot tell within many million how many molecules will pass in a minute through a tube connecting two flasks of gases of unequal density, while the social statistician can tell within a few thousand how many people will pass in a day through the Hudson tube connecting Jersey City and New York. But now that we have the power to discern and track the individual atom and even electron, Maxwell's argument no longer holds. We can sort out isotopes by their weights and divide electrons according to their velocities. We have, therefore, virtually found the sorting demon which, as Maxwell foresaw, might upset or evade the second Law of Thermodynamics and so bring order out of disorder and work out of uniform temperature.

Maxwell argues that all the atoms of an element must have the same weight, for he says ("Theory of Heat," p. 320):

If the molecules of some substance, such as hydrogen, were of sensibly greater mass than others, we would have the means of producing a separation between molecules of different masses and in this way we should be able to produce two kinds of hydrogen, one of which would be somewhat denser than the other. As this cannot be done, we must admit that the equality which we assert to exist between the molecules of hydrogen applies to each individual molecule and not merely to the average of groups of millions of molecules.

But now that Harkins has been able to separate hydrochloric acid gas into denser and rarer portions by simply passing it through a series of church-warden tobacco pipes, Maxwell's argument proves the reverse of what he thought.

Energy, like matter, has come under the atomic theory, and here, too, we are becoming acquainted with its individual units. As Millikan catches and counts the electrons on suspended droplets, so Silberstein catches and counts the quanta of light on Trivelli's silver bromide crystals. A single quantum of light knocks out an electron from a molecule and so disturbs the equilibrium of the salt that the whole crystal can be reduced to the metallic state by a developer. A faint light hits only a comparatively few crystals here and there upon the sensitive plate. A longer exposure hits some more. So Silberstein concludes that light comes like scattered raindrops, not in a continuous stream. I gather from this that we should not speak of "a flood of light," for according to Silberstein it never pours but it rains.

Possibly these wavy arrows of actinic rays, which knock off electrons so easily when they hit a metallic target, may instigate in the same way other or all reactions started by light. This may be the signal that starts the machinery going in the carbohydrate factory of the green leaf. If so, we may learn to better nature in this business as we have in others and set up solar engines of our own.

The chemist provides the motive power of the world, the world of man, not the inanimate globe. Archimedes said he could move the world if he had a long enough lever. The chemist moves the world with molecules. If he can only get control of the electron, he will be in command of unlimited energy. For in this universe of ours power seems to be in inverse ratio to size and the minutest things are mightiest.

When we enter the realm of intra-atomic chemistry, we get behind the elements and may effect more marvelous transformations than ever. The smaller the building blocks the greater the variety of buildings that can be constructed. The chemistry of the past was a kind of cooking. The chemistry of the future will be more like astronomy; but it will be a new and more useful sort of astronomy such as an astronomer might employ if he had the power to rearrange the solar system by annexing a new planet from some other system or expediting the condensation of a nebula a thousand times.

But if the chemist is to become an electron astronomer, he will have to become a mathematician of the highest order. He may even have to enter the fourth dimension. In the good old days a chemist did not have to know any mathematics but arithmetic and that only as far as percentage and the rule of three. He had nothing harder to do than to figure out his analyses so as to add up to 100 per cent, and he did not dare to bring them out exactly to 100 because that would look suspicious. But some twenty years ago it became apparent that the chemist could not keep up with the progress of his science unless he passed in mathematics beyond the eighth grade. It was then that I dropped out of chemistry and took to journalism, a field that so far has not been invaded by the mathematician.

The constructive chemist must often begin by destruction. He must shatter this sorry scheme of things in order to remold it nearer to his heart's desire. To effect the disintegration that must precede the reintegration, the most useful agencies are high temperature and pressure.

THE FUEL PROBLEM

The strike has brought home to us the fuel question—since it does not bring home the fuel. The expansion of population and the development of civilization, even their maintenance at the present standard of life, depend upon finding new and perpetual sources of mechanical energy. The paramount importance of this question has been recognized by the International Research Council, which at its Brussels' meeting on July 25 adopted, as one of three subjects for coöperative study by the twenty nations represented, the investigation of the energy supply of the world. This was a project recommended by the National Research Council of the United States, which presented a plan for the systematic survey of all possible and conceivable means of obtaining mechanical power for the purpose of ascertaining which seem sufficiently adequate and feasible to warrant special research. In this international investigation of the dynamic foundations and future of our civilization, the AMERICAN CHEMICAL SOCIETY is qualified to take a leading part. No achievements would be better worth our \$25,000 prize than a discovery opening up a new source of mechanical energy.

All our food and all our fuel, all our muscular and machine power, depend upon the peculiar ability of the little green granules of vegetation to build up carbohydrates out of air and water. The green leaf reaction—or, if you insist upon having it in Greek, the chlorophyl reaction—is the sole support of all plant and vegetable life and without it the earth would be a desert planet like the moon.

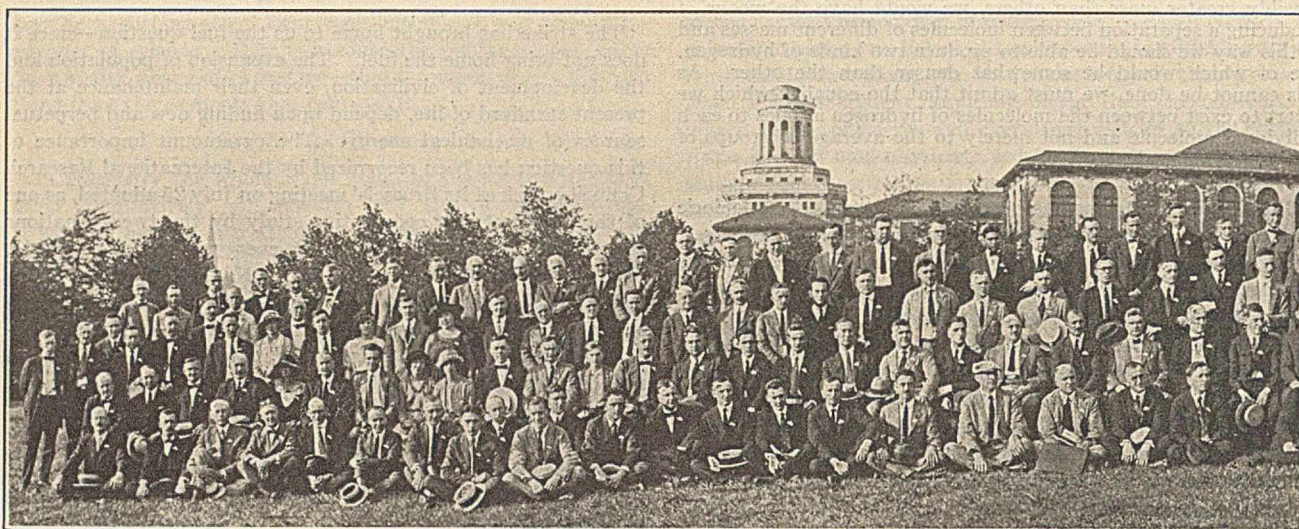
If the work of the world were really done by "horse power," as we still call it, man would have reached the limits of civilization a hundred years ago, for a horse requires hay and hay requires land and there would not be enough land in the world to provide for the horse power we are now using. Supplementing the green fields with the coal fields, man has not only prevented civilization from coming to a stop, but has given it an unprecedented forward impetus. The iron horse feeds on subterranean pastures. He is living on crops of the Carboniferous Era. Modern civilization basks in the sunshine that fell upon the earth unmeasured millenia ago. We are living on our capital, drawing on the coal banks. Sometime we must begin to earn our own living, to grow our fuel as we go.

Meantime, the amount of solar energy that is being stored up in the plants every summer is ten times as great as that released by the combustion of coal. But coal is more condensed and convenient than wood. Oil and gas are still better fuels. It would seriously check the progress of civilization if the world had to return to the wood basis, as it was 150 years ago.

We have been wasting year by year half of our natural gas and three-quarters of our petroleum. The supply of gas has fallen off by a quarter in the last five years, and soon will be running short. Our oil reserves will not last long, fifteen or twenty years at the present rate of consumption is all the geologists will allow us. At any rate the gasoline tank is getting low and no service station is in sight.

Still the trees and tiny plants flaunt their foliage provocatively in the face of the passing scientist, who must confess that he can not yet accomplish what they do so easily—these little green-leaf laboratories, these filmy factories, noiseless, smokeless, odorless, that with no reagents but air and water and no power but the sunshine build up by the ton the most complicated carbohydrates out of the simplest compounds of the commonest elements, carbon, hydrogen and oxygen.

Still, the sun, sole source of all our life and weather, floods half the earth with its rays, and the land that receives the most of this potential wealth is the land that retains the least of it, the arid region of the tropics. A section of the Sahara, forty miles square, receives in six hours a day as much heat as is produced by the coal burned in the twenty-four hours throughout the world. If only a small fraction of this wasted energy could be



economically stored up and set at work by some sort of solar engine, we need not worry about the exhaustion of our oil, gas, and coal. There would be wealth enough for all.

Here, then, is the greatest problem of conservation, the kind of conservation that consists in utilization. But, being accustomed to such wastefulness, it does not excite attention. Nobody is bothering about it except a few chemists, and they do not know how to help it.

Every tiny grass blade points the finger of scorn at the chemist and says "See how we do it. Don't you wish you could?"

And the chemist, with command of pressures varying from a vacuum to the point where steel flows like tar, and with command of temperatures ranging from the boiling point of carbon almost to absolute zero, is still obliged to confess that he cannot accomplish on a commercial scale the simple reaction of the polymerizing of formaldehyde. Even if he knew how, he could not hope to compete with plants on their own ground because they have at their command free raw materials and the cheap labor of protoplasm. Even a professor of chemistry cannot live as cheaply as a cornstalk.

But there are as many celluloses as there are sugars and it is not probable that those that the plants have prepared for their own purposes would be the best for all human purposes. Just as we have found that better dyes and drugs can be made in the factory than can be found in nature, so we may surmise that some of the fundamental foodstuffs—starches, sugars, fats, and even proteins—may possibly be improved upon.

More important and promising than the possibility of synthetic food is the possibility that we may devise some better method of capturing solar energy than the plants have hit upon. We have no reason to assume that the carbohydrates are the only way of solidifying sunshine. The chlorophyll process is shockingly wasteful. Less than one per cent of the solar energy that falls upon a leaf is fixed in the form of carbohydrates, from which it may be later released by oxidation. The crude steam engines, set up in Egypt, catching sunshine by cylindrical mirrors and throwing the heat upon blackened water pipes, have an efficiency of some four per cent, much higher than the green plant.

But a steam engine at best is an inefficient machine, and now that we are able to guide streams of electrons where we will and sort them out according to speeds by means of grids acting like Maxwell's demon, we may reasonably hope to utilize the radiant energy of the sun directly for power purposes. This is not a visionary project such as drawing upon the exhaustless forces inside the atom. That may, for all we know, remain forever

an impossibility. What I am talking about, the fixation of solar energy, is something that we know can be done, for we see it in the grass every sunny day. If sunshine can excite a selenium cell and decompose silver bromide on a photographic plate, it may be made to do work of another sort and on a larger scale. Here, at any rate, is the greatest problem that the world presents, and the highest prizes are offered for its successful solution.

"EXPERIMENTS OF LIGHT"

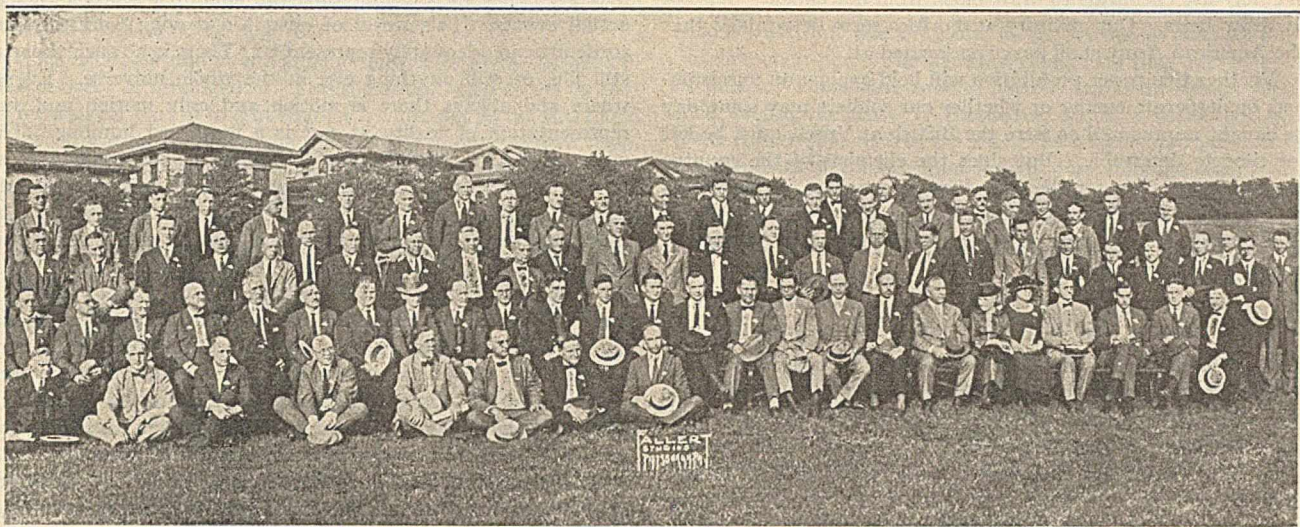
I suppose that all of us have tried erratic experiments that we would not care to confess before our colleagues in such an assemblage as this. Crazy ideas will pop up in the best-regulated brains from some subconscious cellar, and we try them out on Saturday afternoon when there is nobody else around, just to see what will come of them. They do not appear in our published reports—unless they happen to succeed—in which case we claim full credit for our foresight in undertaking an operation that ordinary minds would have condemned in advance as absurd.

Now it is interesting to observe that such irrational experimentation is distinctly recommended by the philosopher who laid down the laws of experimental science that have in the three centuries since accomplished such amazing achievements. Lord Bacon, after listing in his precise and orderly manner all the various ways that we may be guided in our researches by theory, observation, and previous experiment, concludes quite unexpectedly by adding a new category, what he calls the experiments of a madman, and defines as follows:

When you have a mind to, try something not because reason or some other experiment leads you to it, but simply because such a thing has never been attempted before. The leaving I say of no stone in nature unturned. For the magnalia of nature generally lie out of the common roads and beaten paths so that the very absurdity of the thing may sometimes prove of service. But if reason go along with it, that is, if it be evident that an experiment of this nature has never been tried, then it is one of the best ways and plainly shakes the folds out of nature.

The example Bacon gives of such unprecedented experiments is of peculiar interest to us:

But of what I may call close distillation no man has yet made trial. Yet it seems probable that the force of heat, if it can perform its exploits of alteration within the enclosure of the body, where there is neither loss of the body nor yet means of escape, will succeed at last in handcuffing this Proteus of matter and driving it to many transformations; only the heat must be so regulated and varied that there be no fracture of the vessels.



No one should be disheartened or confounded if the experiments which he tries do not answer his expectation. For though a successful experiment be more agreeable, yet an unsuccessful one is oftentimes no less instructive. And it must ever be kept in mind (as I am continually urging) that experiments of Light are even more to be sought after than experiments of Fruit.

What Bacon was "continually urging"—that "experiments of Light," those that lead to enlightenment on fundamental principles, "are even more to be sought after than experiments of Fruit," those that bring practical results—needs more than ever to be kept in mind at the present day, when public and employers are impatient of research that does not bring immediate and profitable returns. So it is worthy of notice that the example which Bacon cites as the experiment of a madman—that is, destructive distillation—has been peculiarly productive of both Light and Fruit. Applied to coal, it has given us coke for metallurgy, gas for cities and shops, and coal-tar products of innumerable variety and inestimable value. Applied to petroleum, it has increased the yield of gasoline by some 2,000,000 gallons a day. By thus "handcuffing this Proteus of matter and driving it to many transformations" we have gained an insight into the structure of the molecule and the chemistry of life.

AN AGENT FOR DEMOCRACY

Chemistry is the most effectual agent for democracy, since it actually accomplishes in regard to many material things that equality which legislation aims to bring about in the political sphere. Luxuries, formerly the monopoly of the privileged classes, become, through applied science, the common property of the masses. The "royal purple" of the ancients and dyes far more beautiful are now to be had on the bargain counter, and Solomon in all his glory was not arrayed like the modern American maiden. Even though her purse be scant she need not lack jewels and perfumes and fine raiment such as once were worth a slave's life. In early ages the man who owned a piece of steel shaped it into a sword and made himself master of his fellows. Now we make buildings out of steel and he who lives in the garret of one of them could look down on the tower of Babel. The Feudal Age vanished at the first whiff of gunpowder, for that device of the Black Art leveled the natural and the artificial inequalities of humanity in warfare, for with a gun in his hand the churl could meet the knight on equal footing and the dwarf was match for the giant—more than a match, for he had the larger target. Medicines such as a prince could not have procured, though his physicians surveyed the earth from China to Peru, are now at hand to cure the pauper. The new chemical

motive powers have given man in the automobile a very fair substitute for the seven-league boots of the fairytale; they enable him to go down into the sea in ships on more or less lawful occasions, and they have endowed him with the wings that he has always longed for but never expected to get until he reached Heaven. Books are no longer chained up in treasuries but, manifolded by the magic of ink, are to be bought on the street corner like peanuts; pictures from the private gallery of prince or plutocrat are multiplied by the same mechanism and scattered throughout the land. We do not have to pay ten dollars to hear one song by Galli Curci since we can hear her at home with as many encores as we like. Caruso, though dead, yet speaketh. His voice has been embalmed by carbolic acid. Events that few could witness are brought to all of us on the celluloid film. So, whether it be the satisfaction of our material wants or the gratification of our aspiration for art and literature, the chemist acts as the agent of applied democracy. Democracy has been engaged in a struggle for life lasting five years and has emerged triumphant—thanks to the chemist. For war has now become essentially a branch of applied chemistry, carried on almost entirely by chemical weapons and chemical defenses. Germany, regarding herself as the heaven-born leader of mankind in this science, attempted to use it to establish her political supremacy in the world, but in spite of her advantage at the start she was foiled in the end by the democratic nations. She had freed herself in advance from dependence upon the nitrate beds of Chile for her explosives by developing methods of making nitrates from the air.

The war is over and Germany has been relieved by the Allies of the burden of armament that still weighs upon the victorious nations. But Germany, unlike the United States, finds it profitable to proceed with the Haber process even in time of peace. We need have no fear of such a catastrophe as the explosion of Oppau. If the Muscle Shoals plant should blow up now, the loss of life would be considerably less. It is curious to recall that the allied aviators were never able to blow up the Oppau works despite their gallant and persistent attempts, yet now the Germans without outside aid have removed the entire establishment from the earth with the greatest ease. The moral of this is the old maxim, "If a thing is to be done, do it yourself."

The Washington Conference on Reduction of Armament decided to prohibit the toxic forms of chemical warfare but not the explosive. Consequently, we cannot use gases against our foreign foes, though they may be still employed against our own people when disorderly. Even the comparatively mild

lachrymatory and sternutatory gases are officially debarred. We may use chemicals to draw blood from our enemies but not to draw tears. Our military authorities seem determined that the American Army shall never be sneezed at.

Whether this paper prohibition will hold against an unscrupulous or desperate enemy or whether our soldiers may some day be caught unprepared as were the British at Ypres, must be left for time to determine. But since the chemists of the country are not responsible for the risk, they may rejoice in the meantime at being relieved of the distasteful task of devising modes of destruction and concentrate their attention upon the constructive side of their science.

SOCIOLOGICAL INFLUENCE

The chemist is not merely a manipulator of molecules; he is a manager of mankind. His discoveries and inventions, his economies and creations, often transform the conditions of ordinary life, alter the relations of national power, and shift the currents of thought, but these revolutions are effected so quietly that the chemist does not get recognition for what he accomplishes, and indeed does not usually realize the extent of his sociological influence.

For instance, a great change that has come over the world in recent years and has made conditions so unlike those existing in any previous period that historical precedents have no application to the present problems, is the rapid intercommunication of intelligence. Anything that anybody wants to say can be communicated to anybody who wants to hear it anywhere in all the wide world within a few minutes, or a few days, or at most a few months. In the agencies by which this is accomplished, rapid transit by ship, train or automobile, printing, photography, telegraph, and telephone, wired or wireless, chemistry plays an essential part, although it is so unpretentious a part that it rarely receives recognition. For instance, the expansion of literature and the spread of enlightenment which put an end to the Dark Ages is ascribed to the invention of movable type by Gutenberg, or somebody else, at the end of the 14th century. But the credit belongs rather to the unknown chemist who invented the process of making paper. The ancient Romans stamped their bricks and lead pipes with type, but printing had to wait more than a thousand years for a supply of paper. Movable type is not the essential feature of printing, for most of the printing done nowadays is *not* from movable type, but from solid lines or pages. We could if necessary do away with type and press altogether, and use some photographic method of composition and reproduction, but we could not do without paper. The invention of wood-pulp paper has done more for the expansion of literature than did the invention of rag paper six hundred years ago.

For the conveyance of ideas the picture is often more effective than the word and here the photographic processes of multiplication due to the chemist are the essential factors.

It is interesting to live at a time when we can witness the birth of a new art. Such was the last quarter of the fifteenth century when the art of printing books was being developed. Such is the first quarter of the twentieth century when the art of depicting motion is being developed. In fact, the moving picture has a better title to the term "a new art" than had printing, to which it was applied so long ago. Printing was not so much a new art as a mechanical extension of an old art, one of the oldest and best developed of the fine arts, the art of calligraphy. The first printed books were but cheap and inferior imitations of the handsome handwritten volumes of that day. Even to-day with four hundred and fifty years of progress it is in cheapness and convenience rather than beauty that the modern book surpasses the ancient manuscript.

Now in the same way the moving picture does for the drama what printing did for literature, that is—it brings it within reach of the multitude through a process of mechanical manifolding.

But it does something vastly more important than this. It makes possible for the first time the unlimited reproduction of actual events. This world of ours is a moving world and no static art can adequately represent it. There is no such thing as still life, or still anything else in the whole universe. Everywhere and always there is motion and only motion and any representation of reality at rest is a barefaced humbug. The more realistic the painting or sculpture the more obvious the failure. Myron's "Discobolus" and Meissonier's "Friedland" are as unnatural and fictitious as a centaur or a hippogriff. The most beautiful painting ever put on canvas, the finest statue ever carved, is a ridiculous caricature of real life compared with the flickering shadow of a tattered film in a backwoods nickelodeon. We have now for the first time the possibility of representing, however crudely, the essence of reality—that is, motion. Bergson has shown us what a paralyzing influence static conceptions of reality have had upon the history of philosophy and how futile have been all attempts to represent movement by rest. The scientist of to-day thinks in terms of motion. All modern thought is assuming kinetic forms and we are coming to see the absurdity of the old ideas of immutability and immobility. A similar revolution is impending in art. At least we glimpse the possibility of a new form of pictorial art, which, if capable of development as it seems to be, will make our present pictures appear as grotesque as the reliefs carved on Egyptian tombs or the scrawls on the caverns of Altamira. What will our posterity, familiar with moving portraiture, think of our admiration of Mona Lisa's smile, frozen on her lips for four centuries? A smile is essentially a fleeting thing, an evanescent expression. A fixed smile is not a smile at all but a grimace. It is only by the most violent effort of the imagination that we can ignore the inherent artificiality and limitations of painting sufficiently to get from it the illusion of reality.

METAPHYSICS OF CHEMISTRY

In considering the contributions that chemistry has made to our wealth and comfort, we must not forget that every fundamental discovery alters also our attitude toward life and consequently our conduct. There is a metaphysical as well as a physical side to chemistry. The new conceptions of the atom and of the sidereal universe, of matter and energy, of time and space, developed within the last ten years, will inevitably transform the prevailing modes of thought in philosophy, religion, and sociology as much as did the Copernican idea of the moving earth in the fifteenth century and the Darwinian idea of developing species in the sixteenth century.

The theory that the heat of the stars comes not from gravitational contraction but from such intra-atomic sources as the formation of helium from hydrogen has extended the life of our sun by some thousands of millions of years, and thereby the limitation of life on the earth and the possibility of the development of a superior civilization. So we don't have to hurry so hard as we did when we thought that the sun was a guttering candle, likely soon to flicker out and leave us in the dark and cold. We used to watch with anxiety the periodical reports of Langley and Abbot as to the constancy of the solar constant in order to see how much more time we had to perfect our social system before night, for when we looked at the daily papers we did not seem to be making progress very rapidly and it looked as though we should all be Eskimos before we got our society to suit us.

The mind is supposed to be immaterial but it seems to be possessed of inertia. The more quickly you want to move the mind of man the greater the power that it is necessary to apply. To move the mental mass of the nation greatly requires almost infinite expenditure of energy or almost infinite time. Since scientific men devote very little energy to the propagation of their views, it takes a very long time for new scientific ideas to

act upon the popular mind. There is consequently a lag in the progress of civilization, a break in the line of march between the vanguard and the rank and file.

This is largely due to the lack of efficient terminal facilities in the delivery of intelligence. Transportation experts tell us that often a larger part of freight charges is consumed in the short haul between station and home than in the long haul by ship or train. So it is in the transmission of ideas. An idea may be sent around the world at the rate of 186,000 miles a second, but the short haul between the eye or ear and the brain may require twenty years. If the message is in a foreign language, such as scientific terminology, and there is no translator about, the reception of the intelligence by the average mind may be indefinitely delayed.

NEED FOR POPULARIZATION

Chemistry has long since abandoned the pretension of being a secret science but it has not yet become a public science. It has the air of being much harder to understand than it really is. Its symbols are almost as repellent to unfamiliar eyes as are the mathematical signs of physics. The verbal formulas, by which compounds are designated, are mistaken for names and considered unpronounceable. But such impediments to popularity are not peculiar to chemistry. Other sciences, quite as much handicapped by strange nomenclature and recondite conceptions, are nevertheless read with eagerness by the public. Astronomy, which is largely mathematical and has no practical value for the reader and does not deal with human beings or any living thing, is still one of the most popular of the sciences. We have to put an astronomical article into our Science News Bulletin every week to satisfy the newspapers to which it is syndicated, but if we omit a chemical article we get no complaints.

One reason why the public is not so much interested in chemical research as it ought to be is the lack of writers willing to translate the science into ordinary English and present it in an attractive style. I speak with some assurance on this point for it has been my business, ever since Science Service was founded a year and a half ago, to hunt for people trained in the several sciences who can and will write about them for newspapers and magazines, and I have found it more difficult to get good writers in chemistry than any of the other sciences. Yet there are more chemists in the country than any other scientists. Not all of them are so absorbed in research, teaching, or industry, that they could not find a leisure hour for writing once in a while. I can find plenty of people to write about birds or bugs, clouds or stones, crinoids or endocrines, stars or starfish, but I find few who will tell the thrilling continued story of chemical discovery.

Yet no science touches human life more intimately than chemistry. None is of more practical importance in industry. None is turning out more sensational novelties. None has a more varied and romantic history.

Of its technical literature chemistry may well be proud. The three journals of this SOCIETY, and especially our system of abstracts, are the envy of all the other sciences, and there are various other able and attractive journals of chemical science and industry. But these are read exclusively by chemists and there is no popular periodical of chemistry published anywhere in the world. In the popular science periodicals and in the scientific articles of the general magazines, chemistry does not fill as large a space as its practical importance and intrinsic interest demands. At least so it seems to a chemist. The chemical news service of this SOCIETY is doing a splendid work in spreading chemical information through the newspapers, and the Local Sections are bringing our science to the attention of the public by their meetings, but there is need for other kinds of chemical literature, especially for magazines and books. Last year the Washington Academy of Sciences prepared, at the request of the Washington Public Library, a list of One Hundred Popular Books in Science.

In many fields, such as botany, astronomy, paleontology, entomology, and the like, there was an embarrassment of books to choose from, but when it came to the science of chemistry Dr. Sosman, chairman of the committee, reported that not one could be found. There were several popular books on special topics, such as the chemistry of commerce, industry and everyman's life, but none that treated the science as a whole and satisfied the requirements of the selection, which were that the book should be readable by the ordinary reader, not a textbook, not a reference book, not a home study course, but so written that it would interest one who had no previous knowledge of the subject and no special reason for wanting to know about it. It is worthy of note that the committee had to go abroad for some forty per cent of its popular science books, and that several of them were over fifty years old, although a recent book would be preferred. Yet some of these British books find their greatest sale in the United States, notwithstanding the advantage that an American writer has in local references and colloquial language. It would seem that a hundred million readers might reasonably expect to have one popular book in each science once in fifty years in order to keep within sight of scientific progress.

I would not take up so much of your time with my business, but it is your business too—at least I hope to persuade you that it is. I am glad to see that you have already taken a step that will aid in the popularization of the science by organizing a Section of History of Chemistry. For one of the reasons why science is caviar to the general, is that it has been so conscientiously depersonalized. The effort is constantly made to reduce science to a set of mathematic formulas, free from all taint of time, place, and personality, bearing no trace of its erratic history and early gropings in the dark. This is quite a proper procedure for the development of the science, no doubt, but it has the unfortunate effect that in eliminating the human element you have eliminated the human interest. C. P. sucrose is a beautiful product, a triumph of technology in which the Division of Sugar Chemistry may well take pride, but it is not so tasty as maple sap or cane juice. It has lost its vitamins. That, I think, is why pure science is distasteful to the layman. It has lost its vitamins. To put a modern high-grade textbook in the hands of the ordinary reader is like feeding decorticated rice to a soldier. It gives him mental beriberi. I hope I will not be misunderstood as saying anything against the chemist's constant efforts to achieve a higher degree of purification. Perfect purity is a noble aim even though it be asymptotically unattainable to human beings. There was once a little girl who prayed "O God, make me pure; make me absolutely pure like Royal Baking Powder!" Now it does not do any harm for baking powder to be pure because it gets mixed with so many other things, but if the flour is absolutely pure, and the fat and the salt and the water, well, somehow the bread is not so nutritious as it might be.

I am not sure that even in a textbook a bit of history or a few personalities would be out of place, though they might give the student the idea that the principles of the science have been worked out by slow degrees and much blundering by fallible human beings instead of being handed down in perfect form on tables of stone like the Ten Commandments. But anyhow, I am sure that for the general reader it is best not to refine too highly but to leave in a little of the human alloy. And I hope that your Section of History will develop some young writers who will turn out a readable character sketch of the creators of chemistry, or a dramatic description of how their discoveries were made and what they mean to the world. One can get such "human interest stories" in abundance about authors, artists, musicians, statesmen, and warriors, but I have been searching in vain for writers who would do as much for science. Until such writers are found we cannot expect readers in general to take as much interest in science as they do in literature, fine arts, politics, and war.

The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine

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AN EXTENSIVE study of gaseous detonation has been made by a number of investigators, but in spite of this fact the phenomenon is as yet not well understood. In presenting this paper, therefore, we will not attempt to explain all the phenomena with which it deals. The object of the paper is to discuss the bearing of this factor on the operation of internal-combustion engines, and to describe the progress that has been made in controlling it by chemical means.

RESULTS OF EARLY STUDY OF GASEOUS DETONATION

In 1881 Bertholet² and LeChatelier³ independently discovered that the propagation of flame through mixtures of some combustible gases with air, and through mixtures of practically all combustible gases with oxygen in proper proportions, results in setting up a detonation wave. These results were confirmed by H. B. Dixon,⁴ who has carried out quite an extensive investigation of this subject. Mallard and LeChatelier⁵ noted that the development of the detonation wave is not progressive, but always instantaneous. They noted further that the detonation wave is characterized, not only by its great velocity of movement, but also by its intense luminosity. Dixon⁶ was also impressed by the sharpness with which luminosity is set up when detonation occurs. Bertholet and Vieille⁷ and also Dixon⁴ showed that the velocity of the detonation wave is constant, and Dixon advanced the theory that during detonation the flame travels at the same speed as sound at the temperature of the burning gases. Mallard and LeChatelier⁷ found that very large pressures are developed by detonation waves, but that such pressures exist only for an exceedingly brief period. This finding was confirmed by Dixon,⁴ who worked on the principle that, if a pressure is produced in a glass container greater than the glass will withstand, the vessel will be broken, although the pressure may endure only for a very short interval of time. Dixon gave a range of from 25 to 78 atmospheres for the magnitude of these pressures for various gases. He showed further that these instantaneous pressures are approximately four times the maximum "effective pressure" developed by the explosion.

GASEOUS DETONATION AN IMPORTANT FACTOR IN INTERNAL COMBUSTION

Except for some comparatively recent work, practically all the study of gaseous detonation that has been made has been conducted in atmospheric tubes, or under other conditions that did not simulate those of internal combustion. From an economic standpoint, however, the detonation that occurs in internal-combustion engines is of great importance.⁸ Nearly everyone

who has driven an automobile is familiar with the troublesome "pinking" in the engine which is known as a "knock." The knock is a sharp ringing noise, suggestive of two metallic parts striking together, and is most pronounced when the engine is pulling at slow speeds in high gear, as is the case on steep grades or when accelerating from slow speeds. This noise is not caused by the striking of metallic parts, but it has been fairly well established that it results from a detonation of the highly compressed fuel mixture in the combustion chamber.

For any given fuel the intensity of detonation varies with the compression of the engine—the higher its compression the more pronounced the detonation. It is herein that the seriousness of detonation in internal-combustion engines lies, for both the torque and the fuel economy of an engine are increased as its expansion ratio (called in automotive practice "compression ratio") is raised. While the detonation that occurs in automobile engines of present compressions is so slight as to be merely an unpleasantness that does little or no harm, in engines of highly economical compressions its intensity becomes so great as to result not only in loss of power but also in actual damage to the engine. This phenomenon of detonation, then, stands as an effective barrier to the obtaining of better fuel economies from internal-combustion engines, and because of this fact, it has an important economic aspect.⁹

Detonation as it occurs in internal combustion does not vary with the compression of the charge alone. It varies directly with the temperature, and is aggravated by advance of the spark timing and by carbon deposits in the engine. It is further influenced by certain elements of design, such as the shape of the combustion chamber and the location of the spark plug, but of great importance is the fact that it is a function of the chemical structure of the fuel. As an illustration of this the case isomeric compounds ether and normal butyl alcohol may be cited. These compounds may have the same ultimate composition, $C_4H_{10}O$, but they differ widely in molecular structure. Ether detonates when burned at a very low compression; alcohol, when burned at a compression and temperature which are relatively very high, is entirely free from detonation. Similarly, ethylenic hydrocarbons have a greater tendency to detonate than saturated cyclic hydrocarbons of the same ultimate composition.

While these facts are interesting and important, the situation with respect to automotive fuels in the United States is that their composition is fixed within fairly narrow limits. From the standpoint of available supply, petroleum oils must be used as the principal source of motor fuels for many years to come. From a commercial standpoint, therefore, the problem is to find a means of controlling the detonation of paraffin hydrocarbons, a tendency which becomes more pronounced as their molecular size increases, or their volatility decreases.

The Automobile Engineer (England), 11 (1921), 51, 92, 130, 169; *J. Soc. Automotive Eng.*, 10 (1922), 305. Thomas Midgley, Jr., *Trans. Soc. Automotive Eng.*, [2] 15 (1920), 659; *J. Soc. Automotive Eng.*, 10 (1922), 357. T. Midgley, Jr., and T. A. Boyd, *Ibid.*, 10 (1922), 7, 451; *THIS JOURNAL*, 14 (1922), 589.

⁹ For a more complete discussion of this phase of the subject see "The Application of Chemistry to the Conservation of Motor Fuels," Midgley and Boyd, *THIS JOURNAL*, 14 (1922), 849.

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² *Compt. rend.*, 93 (1881), 18.

³ *Ibid.*, 93 (1881), 145.

⁴ *Phil. Trans.*, 184 (1893), 97.

⁵ *Ann. Mines* (8th series), 4 (1883), 274.

⁶ *Phil. Trans.*, 200 (1902), 315.

⁷ *Ann. chim. phys.*, 28 (1883), 289.

⁸ Some of the published reports of work done on detonation from the standpoint of the problem as it applies to internal combustion may be found in the following references: Harold B. Dixon, *J. Soc. Automotive Eng.*, 9 (1921), 237; *Automotive Industries*, February 3, 1921, p. 211. Woodbury, Lewis, and Canby, *J. Soc. Automotive Eng.*, 8 (1921), 209. H. R. Ricardo,

THEORIES OF DETONATION IN INTERNAL COMBUSTION

In spite of the fact that gaseous detonation is not well understood, many theories have been advanced to explain the phenomena that occur in internal-combustion engines variously known as "detonation," "knock," and "pinking." Aside from those which may be classified as mere speculations, three theories have been advanced in definite form.¹⁰

The first of these, known as the mechanical knock theory, explains the sound as resulting from an actual impact between parts of the engine, such as between cylinder wall and piston or between shaft and bearings. This theory does not attempt to explain the cause of pressures which must exist in the engine cylinders to produce these mechanical impacts. For this reason it may be passed over with this simple mention.

A second theory is that which explains the sound and attendant phenomena of detonation as resulting from a very rapid increase of pressure in the engine cylinder.¹¹ According to this theory, a portion of the charge is compressed to its auto-ignition point by the expansion of the portion first ignited, which compresses before it the unburned part of the charge. When the rate of increase in temperature due to this compression exceeds by some margin the rate at which a sufficient amount of the heat can be dissipated to the cylinder walls, the remaining portion ignites spontaneously and nearly simultaneously throughout. This theory apparently implies that a fuel should have a tendency to knock that is proportional to its spontaneous-ignition temperature.

The third theory explains the phenomena incident to the fuel knock as resulting from the impact of a high-velocity, high-pressure wave against the cylinder walls and head. It has previously been demonstrated mathematically that, during the passage of a flame through a combustible mixture in a closed container, a higher pressure must exist immediately in front of the flame front than behind it, and that this pressure difference may be represented by the following expression:¹²

$$P_1 - P_2 = \frac{W^2}{g} (V_2 - V_1) \quad (1)$$

where P_1 is the pressure in front of the flame

P_2 is the pressure to the rear of the flame

W is the reaction velocity expressed in pounds of mixture entering the flame front per second

g is 32.2

V_1 is the specific volume of the mixture in front of the flame

V_2 is cu. ft. per lb. of burned mixture to the rear of the flame front

Physical chemistry tells us that

$$W \text{ should equal } CD^n T^m \quad (2)$$

where C is a constant

D , density of the mixture

T , absolute temperature

n , exponent the numerical value of which depends upon the chemical equations of combustion

m , exponent the numerical value of which must be determined experimentally

By combining Equations 1 and 2 and substituting thermodynamic equivalents, the following equation is obtained:

$$P_1 - P_2 = \frac{AP_1^q}{P_1 - P_2} + BP_1^n - CP_2 \quad (3)$$

where $A = 2JHL$

$J = 778$

$H =$ effective heat value per pound of mixture

$$L = \frac{W_0^2}{P_0^q \times g}$$

$$W_0 = KD_0^n T_0^m \quad q = \frac{2[n + m(\gamma - 1)]}{\gamma}$$

$$g = 32.2$$

$$B = \frac{2K \frac{1}{\gamma} L}{\gamma - 1}$$

$$K = \text{constant of adiabatic compression} \\ = P_1 V_1^\gamma$$

$$N = q - \frac{1}{\gamma}$$

$$C = \frac{2\gamma}{\gamma - 1}$$

$\gamma =$ ratio of the specific heats

This Equation 3 should represent the relation between the pressure in front of the flame and that to its rear at all times. It is, therefore, an expression for the pressure in the wave of detonation ($P_1 - P_2$). Values for n and m must be determined experimentally for each different fuel. But, if values be ascribed to n and m , and the relation of P_1 to P_2 be plotted, it will be observed that below some critical value for P_2 the pressure difference is merely nominal, but that at this critical value P_1 is rising at an infinite rate. Above the critical value for P_2 the equation is only satisfied by $P_1 =$ infinity, which in a physical sense means a large difference of magnitude such as 50 to 100 times P_2 .

The above Equation 3 affords a basis for the explanation of the phenomena incident to detonation. During normal combustion the pressure differential is almost insignificant, its magnitude being less than one pound per square inch, but in the case of a flame front moving at the velocity of sound with respect to the burning gases, the pressure differential becomes enormous. If $P_1 =$ infinity, P_2 may be any value large or small, so that during detonating combustion the flame front is preceded by a region of dense gas at an extremely high pressure. According to this theory, the metallic sound, commonly called the knock, is caused by this high-pressure, high-velocity wave striking the top or sides of the combustion chamber.

If the second or auto-ignition theory gives a correct explanation of detonation, the only means of controlling detonation under a given set of conditions would be to raise the spontaneous-ignition temperature of the fuel. If the third or high-velocity, high-pressure wave theory is correct, detonation may be controlled by affecting the reaction velocity of combustion. The history of contact catalysis indicates that there should be negative combustion catalysts, very small percentages of which would exert a large effect on the reaction velocity of combustion. Although such a method of reasoning might well have served as the basis of search for a material to negatively catalyze combustion, the actual discovery of materials that exert just such an effect preceded the development of the high-velocity, high-pressure wave theory, it having been an outgrowth of many attempts to explain the remarkable behavior of these substances. In view of the very small amounts of some compounds that need be present in a combustible mixture in order to prevent detonation, as is shown below, it does not seem possible to account for their behavior on the basis of the auto-ignition theory of the knock. However, on the basis of a negative catalytic effect on the reaction velocity of combustion, the behavior of the materials discussed in this paper is in agreement with the high-velocity, high-pressure wave theory of detonation.

CONTROLLING DETONATION BY CHEMICAL MEANS

It has been found that detonation can be either suppressed or induced by the presence of very small amounts of certain materials in the combustible mixture. These substances may be dissolved or suspended in the fuel, or they may be admitted to the combustion chamber in some other way. The action of practically every type of compound that should affect detonation

¹⁰ Dickinson, *J. Soc. Automotive Eng.*, **8** (1921), 558.

¹¹ H. R. Ricardo, *The Automobile Engineer (England)*, **11** (1921), 92; *J. Soc. Automotive Eng.*, **10** (1922), 308.

¹² T. Midgley, Jr., *J. Soc. Automotive Eng.*, **10** (1922), 361.

has been tried, and a large number have been found to possess the property of affecting combustion in such a way as either to suppress or induce detonation.

TABLE I

ELEMENT	TYPICAL COMPOUND	EFFECT ON REACTION VELOCITY OF COMBUSTION
Iodine	Element	Retards
Bromine	Element	Accelerates
Oxygen	Element	Accelerates
Oxygen	$C_2H_4NO_2$ or $C_2H_5NO_2$	Accelerates
Nitrogen	$C_2H_5NH_2$	Retards
Selenium	$(C_2H_5)_2Se$	Retards
Tellurium	$(C_2H_5)_2Te$	Retards
Tin	$(C_2H_5)_4Sn$	Retards
Lead	$(C_2H_5)_4Pb$	Retards

If the high-velocity, high-pressure wave theory of detonation is correct, the action of these materials is to affect the reaction velocity of combustion in such a way as either to accelerate or retard the tendency of the combustion to reach the velocity of detonation. Because of this effect, substances which, when present in small percentages, exert a powerful suppressing action on detonation have been termed "antiknock materials" or "compressionizers." Thus, diethyl telluride is an antiknock material, but benzene is not. Although benzene, if present in sufficient concentration, removes the tendency of kerosene to detonate at compressions which are used commercially, it apparently does so simply by virtue of the fact that it itself is a fuel that will withstand a very high compression without detonating. Benzene does not detonate even when burned at compressions of more than 200 lbs. per sq. in., so that, when it is blended with a kerosene, the resulting mixture partakes of the non-detonating property of benzene to the extent to which benzene is present in the mixture. This is evidently not the case with diethyl telluride, however, of which 0.1 per cent by volume is equivalent in its effect on detonation to about 25 per cent by volume of benzene. Diethyl telluride exerts this remarkable influence on the combustion of a kerosene-air mixture, although in this case it is present in only the very small ratio of 1 molecule to about 50,000 molecules of total mixture.

It is not within the scope of this paper to present detailed data on all the antiknock materials that have been studied, especially since the investigation has not been completed, but the results that have been obtained may be summarized in general terms.

TABLE II—A COMPILATION OF THE RELATIVE EFFECTS OF A NUMBER OF COMPOUNDS FOR SUPPRESSING DETONATION AS COMPARED WITH BENZENE

ELEMENT	COMPOUND	Per cent by Volume in Kerosene Required to Effect a Given Suppression of Detonation	Number of Gram Molecules in Resulting 355-Cc. Mixture with Kerosene to Give Equal Suppression of Detonation	Approx. Number of Mols of Theoretical Fuel-Air Mixture in Which 1 Mol Exerts an Effect on Detonation of a Given Magnitude ¹
	Benzene	25.0	1.0 ²	150
Iodine	C_2H_5I	1.6	0.07	2,150
Nitrogen	Xylidine	2.0	0.059	2,600
Tin	$(C_2H_5)_4Sn$	1.2	0.021	7,100
Selenium	$(C_2H_5)_2Se$	0.4	0.013	11,750
Tellurium	$(C_2H_5)_2Te$	0.1	0.003	50,000
Lead	$(C_2H_5)_4Pb$	0.04	0.0007	215,000

¹ The computations of these values have been made on the basis of a kerosene having $C_{15}H_{32}$ as its average molecule.

² 25 per cent by volume.

The compounds which have been shown to possess this property of affecting the reaction velocity of combustion to a marked degree are chiefly derivatives of about fifteen elements, but we have found that antiknock substances are not limited entirely to compounds of these fifteen elements. Oxygen and the halogens in the elemental form exert a marked effect on combustion, iodine being an antiknock material, and the other elements inducing detonation to different degrees. A considerable number of the common compounds of these elements exhibit similar properties. A great many nitrogen compounds are effective antiknock materials, probably the best of which are the aromatic amines. Certain compounds of selenium, tellurium, tin, and lead, are remarkably effective for the suppression of detonation. Some compounds of arsenic, antimony, and phosphorus have a marked but lesser effect for preventing detonation. Table I

shows the nature of the effects of some of the more important of these substances on the reaction velocity of combustion.

A compilation of the relative effects of a number of antiknock materials is given in Table II. Benzene is used as a basis of comparison, and relative values are given for the various materials on the volume and the molecular bases. From the table it may be seen that, when compared with benzene in 25 per cent concentration in kerosene, 1 volume of diethyl telluride is equivalent in effect to 250 volumes of benzene, and 1 volume of lead tetraethyl is equivalent to about 625 volumes of benzene. If comparison be made on the molecular basis, the figures show that 1 molecule of diethyl telluride is equal in effect to 330 molecules of benzene, and that 1 molecule of lead tetraethyl is equivalent in effect to over 1400 molecules of benzene. A better impression of how small an amount of some of these materials need be present in a combustible mixture in order to exert a marked influence on the character of the combustion may be gathered from the values given in the last column of Table II. Thus, for a theoretical mixture of kerosene and air, assuming that the average molecule of the kerosene is $C_{15}H_{32}$, 1 molecule of lead tetraethyl in 215,000 molecules of total mixture exerts an influence on the tendency of the fuel to detonate which is equivalent to about 25 per cent of benzene in the kerosene. In view of the exceedingly small amount of this material that is present in the reaction mixture, it exerts an influence on the character of internal combustion, which is so powerful that it at least bears a close analogy to a catalyst.

ILLUSTRATIONS OF EFFECTS OF ANTIKNOCK MATERIALS ON DETONATING COMBUSTION

The effect of the presence of a small percentage of diethyl selenide on the combustion of a detonating mixture of acetylene and air is very marked. An apparatus suitable for demonstrating this effect is shown diagrammatically in Fig. 1. The diameters of the gas holders bear such a relation to each other that a mixture of acetylene and air of proper degree of richness for maximum detonation¹³ is forced into the explosion tube shown at the bottom of the sketch by water flowing from the upper container and displacing the gases from their respective holders. The mixture is formed in the end of the explosion tube where the outlet tubes from the gas holders enter the same chamber. The

mixture passes through this metal chamber which is provided with a spark plug, and thence into the glass explosion tube. The closing of the valve in the chamber at the end of the explosion tube automatically completes the ignition circuit, and thereby ignites the mixture in the explosion tube.

As a means of introducing diethyl selenide to the acetylene-air mixture when desired, the valve in the gas line through the wash bottle is opened. An orifice in the by-pass tube permits a small amount of the air to pass through the wash bottle which contains the vapor of diethyl selenide. At 22° the vapor pressure of diethyl selenide is about one-twentieth of an atmosphere.

¹³ Detonation is said to be most easily initiated in an acetylene-oxygen-nitrogen mixture that contains only sufficient oxygen to give carbon monoxide. Woodbury, Lewis and Canby, *J. Soc. Automotive Eng.*, 8 (1921), 215; H. B. Dixon, *Ibid.*, 9 (1921), 237.

The size of the orifice is such that, when the valve in the by-pass is open, diethyl selenide constitutes about one-seven-hundredth of the volume of the mixture entering the explosion tube. This amount is so small that it cannot affect the combustion by combining with either of the reacting materials, or by entering into the reaction in the ordinary sense.

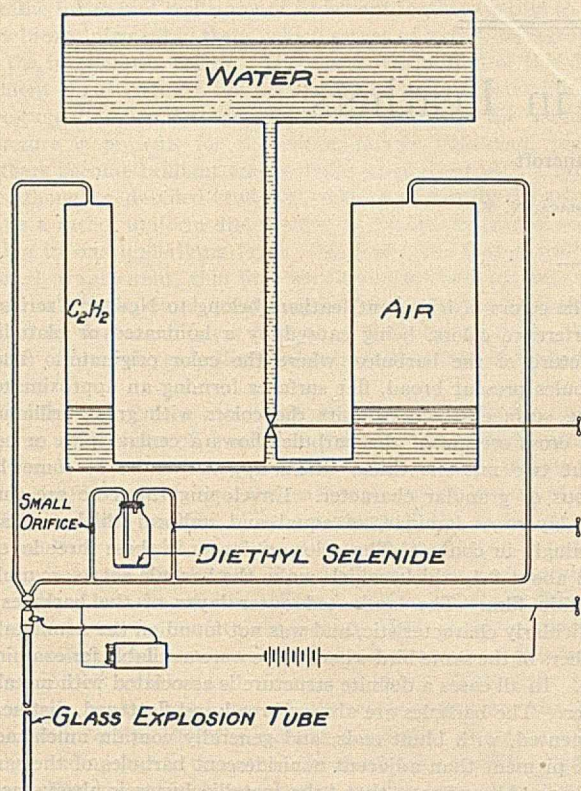


FIG. 1

APPARATUS SHOWING THE EFFECT OF THE PRESENCE OF AN ANTI-KNOCK MATERIAL ON THE COMBUSTION OF ACETYLENE IN A TUBE AT ATMOSPHERIC PRESSURE

The demonstration shows that with acetylene and air alone detonation is set up after the flame has traveled only a short distance along the tube, as is evidenced by the luminosity, and by the sharp "crack" that is produced by the pressure wave resulting from the detonation. But when diethyl selenide is admitted with the acetylene-air mixture, the burn is quiet and it lacks the high degree of luminosity that characterizes detonating combustion.

The effect of the presence of an antiknock material on combustion is even more striking under the actual conditions of internal combustion. A single cylinder engine having a high compression ratio, preferably around 5.3 : 1, is suitable for use in this test.¹⁴ The engine should also be fitted with an apparatus for indicating when the combustion is a detonating one. Such a device, called the bouncing-pin apparatus, has been described and shown diagrammatically in previous publications.¹⁵ The bouncing-pin element consists of a steel pin resting by gravity on a piston. The bottom of this piston comes flush with the inner surface of the cylinder head, and its vertical movement is resisted by a heavy spring. Immediately above the upper end of the pin,

¹⁴ The compression ratio of an engine is the ratio of the volume above the piston when it is in its extreme lower position to the volume above the piston when it is in its extreme upper position. The compression ratio of automobile engines at present is about 4.25 : 1. In this connection attention is again called to the fact that the intensity of detonation increases with the compression ratio of the engine.

¹⁵ Midgley and Boyd, *J. Soc. Automotive Eng.*, 10 (1922), 7, and *THIS JOURNAL*, 14 (1922), 589.

contact points are held in position in an electric circuit in such a way as to be closed when the pin is thrown free of the piston. During normal combustion, when there is no detonation, the pin moves up and down with the piston, the amplitude of movement of which is only a few thousandths of an inch. But when detonation occurs, the disturbance in the combustion chamber is of such a nature that the pin is thrown free of the piston, closing the contact points. This completes the electric circuit, and during the period that the contact points are closed, current flows through the lamp and the electrolytic cell. If the detonation is continuously repeated and of sufficient violence, the lamp filament becomes luminous, but even a slight or discontinuous detonation causes the evolution of gas in the electrolytic cell. The quantity of gas generated in a given number of revolutions is a measure of the intensity of detonation.

When this engine is run on commercial gasoline alone, a violent detonation occurs, which imparts considerable luminosity to the filament of the lamp. The detonation also manifests itself by the loud and sharp metallic sound in the engine, and by the large volume of gas generated in the electrolytic cell. If, while running under this condition, a small amount of the vapor of diethyl selenide (simply that arising from a bottle containing liquid diethyl selenide) be admitted with the air entering the combustion chamber, the detonation is entirely eliminated, and the power output of the engine rises to normal, or to the extent that it had been cut down by the detonation.

If the same engine be run on a mixture of about 35 per cent benzene in commercial gasoline, very little, if any, detonation will be noted. A violent detonation is induced, however, when an unstoppered bottle containing a volatile nitrate or nitrite, such as isopropyl nitrite, is held close to the air inlet of the engine. The intensity of this detonation may easily be made so great as to result in stopping the engine altogether. Bromine may be substituted for the nitrite in this test, but it is only about one-half as effective for inducing detonation.

These materials are equally effective when admitted with the fuel, either in solution in the fuel or by injection along with it. In this engine, having a compression ratio of 5.3 : 1, which gives a compression around 115 lbs. per sq. in., the detonation when running on commercial gasoline alone is so violent that it results in a large loss in the power of the engine. But when a very small amount of tetraethyl lead, around 0.1 per cent by volume, is present in the gasoline, the engine runs with such perfect smoothness that no gas is generated in the electrolytic cell, and the power of the engine comes back to normal. Computation shows that this result is accomplished simply on account of the presence of 1 molecule of lead tetraethyl in over 80,000 molecules of total mixture.

A CONCEPTION OF THE ACTION OF ANTIKNOCK MATERIALS

The action of antiknock materials, such as diethyl selenide or lead tetraethyl, appears to be that of preventing combustion from becoming abnormal by accelerating to the velocity of detonation. It is inconceivable that this effect can be due to an energy factor; because, as has been shown (Table II), the presence of as little as 1 molecule of one of these materials in over 200,000 molecules of a combustible mixture of kerosene and air exerts an effect in the suppression of detonation equivalent to 25 per cent of benzene by volume in kerosene.

These materials appear to have an effect on the chemical reaction, combustion, that is closely parallel to that of the class of substances called catalytic agents. Thus, very small amounts of these substances are required to exert a remarkable influence on combustion. Also, in the case of the most powerful antiknock materials, the effect does not increase indefinitely in proportion to the amount present, but, as concentrations which are relatively high are reached, the curve of effect tends toward an asymptote to a maximum. A further analogy between catalytic agents and

these substances lies in the fact that the antiknock material apparently does not affect the final state of equilibrium, except in so far as by retarding the reaction velocity of combustion it tends to insure its completeness. The analogy breaks down to some extent on the criterion that the chemical composition of the catalytic agent is unchanged at the completion of the reaction

process. However, antiknock materials are for the most part combustible, and the conditions to which they are subjected are extremely severe. On the whole, it appears that the action of these substances, which have been termed Antiknock Materials or Compressionizers, bears considerable analogy to that of catalytic agents.

Iridescent Colors in Feathers¹

By Wilder D. Bancroft

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AT THE Rochester meeting I reported on the structural blues in feathers. That left the metallic or iridescent colors to be accounted for. Michelson² believes that the colors in the tail of the peacock and the throat of the humming bird are due to selective reflection, like the yellowish green metallic color of solid magenta. Lord Rayleigh³ maintains that the colors are the interference colors of thin films, often referred to as Newton's rings. Since the question seemed to involve coöperative research by men representing different fields, the Heckscher Research Council made a grant to a committee consisting of Messrs. Bancroft, Chamot, and Merritt, representing physical chemistry, chemical microscopy, and physics. As an unofficial member representing ornithology, the committee has had the enthusiastic coöperation of Mr. Louis Agassiz Fuertes, who was really responsible initially for the starting of the whole investigation. The work of the committee has been facilitated by the courtesy of Prof. A. A. Allen of Cornell University and of Dr. Frank M. Chapman of the Natural History Museum, who have supplied us with many typical feathers. For the experimental work the committee has been fortunate in securing the assistance of Mr. Clyde W. Mason, assistant in chemical microscopy at Cornell University. It is to his skill and perseverance that the successful outcome of the investigation is due.

While the nonmetallic blues are always in the barbs, the iridescent colors are wholly in the barbules, the barbs in such feathers being a dark dull brown and showing no color effects. The iridescent colors are visible by reflected light from both surfaces of the features but cannot be seen by transmitted light. By transmitted light the feathers of the blue jay, the tail feathers of the peacock and the throat feathers of the humming bird show no more signs of brilliant colors than do the feathers of a crow.

There is not only no bright color to be seen by transmitted light in any metallic or iridescent feather, but no bright-colored pigment can be extracted by boiling with any organic liquid. If the dark or melanin pigment is extracted, the metallic color remains with little change until the dark pigment is practically all gone and can be detected even then when the feather is examined under the microscope. The change in color with changing angle of incidence is that corresponding to interference colors, and is much greater than with substances like magenta, showing selective reflection. In fact, the change of color with changing angle of incidence is practically negligible with magenta and the other pigments of this type. The natural conclusion is, therefore, that the iridescent colors are not due to selective reflection.

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

² *Phil. Mag.*, [6] 21 (1911), 554.

³ *Ibid.*, [6] 37 (1919), 98.

The colors of iridescent feathers belong to Newton's series of interference colors, being caused by a laminated or plate-like structure of the barbules, where the color originates. These barbules present broad, flat surfaces forming an approximately plane surface which exhibits the colors with great brilliancy. The cross section of the barbule shows a central pith or core about two microns thick, which appears to be of somewhat fibrous or granular character. Enveloping this core are three thin layers or laminae, of equal and uniform thickness, and seemingly in contact. The color originates in these three layers, each about 0.4μ thick, which make the barbule act as a multiple thin film. The laminated outer layer of the barbules is particularly characteristic, and was not found on the nonmetallic feathers of the same bird where these were available for examination. In all cases a definite structure is associated with metallic luster. The barbules are always broad and flattened, distinctly segmented, with blunt ends, and generally contain much more dark pigment than adjacent noniridescent barbules of the same feather. Altum⁴ says that "the metallic luster is always associated with the peculiar, hard, and smooth texture. A blind man could easily pick out all the birds with metallic luster in a collection of any size." The relation between structure and metallic luster is so close that Mr. Mason was able to pick out from the collection of drawings of barbules in Chandler's paper⁵ those which were of the metallic type. Comparison with the description of the coloring of the feather showed very few errors, even though the drawings cover almost all species and include many feathers not possessing any noniridescent barbules for comparison.

The thickness of these films is about the value calculated for the interference colors of the order observed in feathers, though the whole structure is too small for very accurate measurements. In all the iridescent feathers examined, the colors appear to lie in the upper second or third orders of the series, which include the most brilliant of the interference colors—yellow, and red in the upper second order, and dull purple, blue, green, yellow, and red in the third order. Since we have no good method of determining exactly the order of interference and isolated color reflected from a thin film, this is based on matching the colors of feathers with those of artificial films, the colors of which are of known order.

With increasing angle of incidence the color usually changes through two or three of the colors of the above series. The change is frequently from the blue to the red end of the spectrum, but this is not necessarily the case. The pigeon, for instance, has feathers which change from bluish green through red to yellowish green with increasing angle of incidence. Thickening of the color-producing films by swelling results in a color change toward

⁴ *J. Ornithologie*, 2 (1854), 19.

⁵ *University of California Publications, Zoology*, 13, No. 11 (1914-16).

a color listed in a series after the original color, for the order of the color is higher the thicker the film. Thinning by pressure or in fault bars results in a color of lower order (earlier in the series) than the original color of the barbules.

Bleaching does not destroy the colors, because there is no bright pigment to be destroyed, but only a structure; and the iridescence is uninjured unless the structure is destroyed. The metallic luster and brilliancy of iridescent feathers is due to the dark brown pigment in them, which serves as a dark background for the interference colors. The exact distribution of this dark pigment is not certain; but apparently no special distribution is necessary to give the metallic luster, provided the essential structure is present, for the white, faintly iridescent, pigeon feathers become brilliant and metallic when dyed with a brown dye, though a detailed study of sections of the dyed barbules shows a rather uniform distribution of the dye instead of segregation in one underlying layer. It is possible that a neutral-colored, transparent, thin film may serve to some extent as its own dark background, producing brilliant colors and a metallic luster, as does a colorless film on a dark background. As a matter of fact, we get brilliant colors with thin films of asphaltum varnish.

The metallic colors can be duplicated very satisfactorily by putting a thin film of a colorless varnish over a dark pigeon's feather, but the result is more garish than the real feather, because the film spreads over the feather as a whole instead of over each individual barbule. The curvature of the barbules, with the resultant complexity of the surface of the feather, results in a softening and blending of the garish colors noticed in plane, thin films, because of the different angles at which different parts of the curved surface are viewed. This causes a mingling of the colors seen at normal and at other angles of incidence, giving added softness and richness of color. The slight local variations in the thickness of the color-producing film also contribute to this effect by causing a mottling of colors, which mingle and appear to the eye as the mean color of all the various hues. The color which we observe on the feather is thus the result of the mingling of a number of colors adjacent in Newton's series, which produce the effect of a single, softer color. No one can deny that the colors of thin oil films on a pavement are garish.

Variation in the thickness of the color-producing films explains the different colors often observed on a single feather, either in the form of a pattern, as in the case of the peacock, or in gradations of color, such as are seen in the feathers of the starling, purple grackle, *Lamprocolius phoenicopterus bispecularis*, and other birds. Such iridescent feathers show bands of colors which remind one very much of the colors produced by oil on an asphalt pavement. For instance, some of the feathers of the starling are iridescent reddish purple at the base shading to yellowish bronze at the tip; others are yellowish green at the base to greenish blue at the tip; while some feathers of the purple grackle shade from reddish purple at the base to blue, greenish blue, green, yellow-green, to yellow-bronze at the tips. These sequences of shades are undoubtedly produced by a gradual variation in thickness of the color-producing films, for the colors adjacent on the feather are always adjacent in Newton's series, and, moreover, the colors shift with increasing incidence, just as do Newton's rings, the shift or change in position of a given color being toward the thicker part of the film.

The grosser structure of the feather may influence the appearance of the iridescent colors very markedly. Not only the perfection of the surface formed by the overlapping of the distal barbules, but also the visibility of the color, are dependent on this. For example, the blue-green iridescent barbules of the peacock feather are present in the black center of the "eye," but are arranged so that they are seen edgewise and their color ordinarily does not appear. The iridescent colors of many birds, particularly humming birds, are often visible only from a

position in front of the bird, and are quite invisible when the head of the bird is pointed away from the observer. This, again, is due to the barbules which are so arranged that, instead of having their planes in the general plane of the feather, they are skewed or tilted somewhat, and lie normal to a direction toward the head of the bird, rather than in the plane of the feather. Consequently, they are seen edgewise from other positions, and give little or no color.

One marvels at the way in which these colors are produced with such uniformity on different feathers and different birds through successive generations, in spite of the fact that a very slight variation in the thickness of the films would alter the color effect greatly. The production of iridescence seems to present a most remarkable case of the regulation of an essential structure within very sharply defined limits, not only in numerous individuals but also through many successive generations. Perhaps more remarkable still is the case of the white peacock. We had hoped that the tail feathers of the white peacock differed from those of the ordinary peacock only in not having the dark pigment present, in which case dyeing the feather or painting the back of it black would bring out the brilliant metallic colors. This does not happen because the tail feathers of the white peacock do not have at all the same structure as those of the ordinary peacock. In spite of the absence of color and the complete difference in structure, the general pattern of the peacock feather has been preserved in the white peacock even though the effect is produced in an entirely different way. This must have some great biogenetic significance, though fortunately that is not a problem for the chemist.

When this work was begun, the committee believed strongly in Michelson's theory of selective reflection; but it was soon found that this theory could not be applied satisfactorily to the phenomena observed, and the conclusion was reached finally that Michelson was wrong and Lord Rayleigh was right. The iridescent colors of feathers are caused by thin laminae or films in the barbules which produce interference colors. No colors due to selective reflection have been detected in any of the metallic feathers which have been studied. The birds examined include:

Black Minorcas and Rhode Island Reds (*Gallus*)
 Bronze-winged Pigeon (*Columbia phaps*)
 Common Pigeon
 Green Heron (*Ardea virescens*)
 Wood Duck (*Aix sponsa*)
 Mallard (*Anas boschas*)
 Sommering Pheasant (*Phasianus sommeringi*)
 Monaul Pheasant (*Lophophorus impeyanus*)
 Golden Pheasant (*Thumalea picta*)
 Chinese Pheasant (*Phasianus torquatus*)
 Peacock Pheasant (*Polyplectrum bicalcaratum*)
 Bronze-headed Trogon
 Peacock (*Pavo cristatus*)
Musciroia mexicana
Ptilopus puella
Ptilopus pulchellus
Lamprocolius phoenicopterus bispecularis
 Purple Grackle (*Quiscalus purpureus*)
 Jacamar (*Jacamarops aureus*)
 Ruby-throated Humming Bird (*Trochilus colubris*)
 Red Kingbird of Paradise
 Wild Turkey (*Meleagris americana*)
Neltion brasiliense
 Starling (*Sturnus vulgaris*)
 Muscovy Duck (*Cairina moschata*)

Chemists in New Jersey have formed a Chemists' Frelinghuysen Club to support Senator Frelinghuysen in his candidacy for reelection. The basis of the appeal is to be his sympathy for and service to the chemical industry.

The Journal Literature of Chemistry

By E. J. Crane

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HUMAN progress is made by coöperation. This is a scientific and industrial age. The great factor for progress in science and industry is research. Coöperation in research is effected chiefly by means of the journal literature. Among scientists, and increasingly among men of industry, there is a notably fine spirit of coöperation and service which prompts the publication for the benefit of all of the results and conclusions from their experiments and experiences. In the production of this literature, in its distribution, and in its use, efficiency is obviously of great importance. There is much room for betterment. The amount of wasteful repetition of thought and effort (some duplication of work to be sure is desirable and profitable) that can be attributed to the slightness of our command of the accumulated knowledge of mankind is exceedingly large. The great need and value of coördinated, available information were discussed with a broad point of view by Dr. Charles L. Reese in his admirable address¹ before the AMERICAN CHEMICAL SOCIETY at Birmingham and the efforts and plans of the National Research Council in its Information Service towards the fulfillment of this need were described. These efforts deserve full support. Dr. Reese dealt with information as a whole and spoke mostly of needs. It is my purpose here to set forth a few more or less random observations from constant work with the journal literature of chemistry, which it is hoped may be helpful to individuals in their efforts to increase their personal efficiency in the use of this literature in its present condition and with available facilities. Skill in this direction is of great value to any chemist. Are not too many lacking in such skill?

To trace in detail the development of the journal literature of chemistry from the period when personal contact and correspondence were the only means of coöperation through the various stages up to the present time, or to attempt to classify this literature, as might be done in several ways, is beyond the limits of this paper. Suffice it to say that since 1665, when the first scientific journal, the *Philosophical Transactions of the Royal Society*, put in its appearance, there has been an accelerated increase in the number of journals of interest to the chemist, and the bulk of the accumulated material has become almost staggering in its proportions. At the present time there are over a thousand journals appearing which have at least some chemical interest. The vastness of the chemical journal literature, its rapid and continuous advance upon the frontiers of our knowledge, and its essentially unorganized state, are further arguments why the chemist should see to it that he learns how best to make use of the means which have been provided to make this sea of information navigable. Otherwise he is likely to be lost at sea.

EXACTNESS IN WRITING

Many chemists are producers as well as users of chemical literature. While it is my purpose to speak chiefly of the use of the literature, may I call attention to one characteristic of chemical papers which our experience in the office of *Chemical Abstracts* leads us to believe ought to be bettered by chemists who write papers? That exactness in scientific work is of paramount importance is not likely to be questioned. The same careful precautions to insure exactness which are taken in their work in the laboratory are apparently not always followed in the reports of their work as written by a good many chemists.

It is a matter of good English and good nomenclature. Sentences which may have more than one meaning and names which do not definitely identify compounds are not infrequent in chemical papers. It is the duty of editors to bring about improvements in this respect. It is nevertheless important that those who write papers watch carefully for such situations and correct them; things get past editors.

It is particularly with reference to the names of chemical compounds that improvement is urgent. The journal literature is full of bad nomenclature. May it not rightly be considered the duty of every chemist who writes a paper to attempt to determine the best name for each compound which he has occasion to mention? Unfortunately, this is not always an easy matter, but it is usually possible. For the commoner compounds Webster's New International Dictionary is a good standard. For inorganic compounds Roscoe and Schorlemmer's "Treatise on Chemistry" (Vol. I, The Non-metals; Vol. II, The Metals), and Mellor's "Modern Inorganic Chemistry" are good. The indexes to the *Journal of the Chemical Society* (London) and to *Chemical Abstracts*, in the preparation of which special efforts have been made to keep the nomenclature good, should be helpful. The AMERICAN CHEMICAL SOCIETY'S Nomenclature, Spelling and Pronunciation Committee is always willing to do what it can to assist. The chemist especially interested in one branch of chemistry is more likely to fail to use proper nomenclature if he has occasion to enter into the special domain of another branch. For example, it is possible to point out comparatively numerous cases in which a physical chemist has made very exact measurements of some property of an organic compound, giving perhaps a figure involving several decimal places, and then in reporting his results has used a name which is indefinite, as that of a compound with isomers without designation of the particular isomer. The use of good chemical nomenclature is really necessary in the use of good English and in that sense is a cultural attainment. Furthermore, some knowledge of good nomenclature is essential if efficient literature searches are to be made.

DISTRIBUTION OF LITERATURE

The distribution of the journal literature is more or less haphazard and uneven. It is often a problem to lay hands on a needed paper after a reference to it has been located. Desired papers may appear in rare journals available only in a few places and many chemists are located far from good libraries. This situation has been helped greatly in recent years by the introduction in most of the larger scientific libraries of a photostat copying service. Photostat copies of papers can now be obtained from a number of centers at a rate which is approximately equivalent to cost. The significance of this comparatively new facility is apparently not fully recognized as yet and full advantage of it has not been taken. Inter-library lending practice, a translating service by a few libraries, and the lending of rare journals, not available elsewhere, by the office of *Chemical Abstracts*, are other means of obtaining papers.

Many are familiar with the list of current periodicals of interest to the chemist which has been compiled in the office of *Chemical Abstracts*. This list, which now contains well over a thousand entries, is being revised and will soon be published again as a supplement to a number of *Chemical Abstracts*. Announcement is made that, in addition to the customary information as to frequency of appearance, number of volumes

¹ THIS JOURNAL, 14 (1922), 364.

per year, price, and publishers' names and addresses, the new list will supply information as to where among the more important libraries of the United States files of the various journals are maintained. Also information will be given in each case as to whether or not a copying, lending, or translating service is maintained by these libraries. Approximately 170 libraries representing all parts of the country will be included. This information on the location of journals has been gathered by the National Research Council. Drs. Harrison E. Howe, Clarence J. West, and Callie Hull deserve credit for providing the instrumentality for effecting this canvass of libraries. With these location data available and photostat service becoming more extensive, the solution of the problem of getting to papers or of obtaining copies should be greatly helped.

INDEXES

The main problem, of course, in using the journal literature is in finding references, all that are pertinent to the subject at hand, in order that one may learn what the literature contains and all that it contains relating to this subject. This is often difficult. It is doubtful if there is a more important problem for students, in college or out, to learn how to solve. Its solution involves to some extent a familiarity with the more important journals, particularly the abstract journals, but above all it involves a knowledge of indexes and how to use them. References to the journal literature are often obtained from books or from one paper to others, but mostly they are obtained from indexes, usually of abstract journals. It is frequently assumed that the use of indexes in making literature searches is a simple matter requiring no special experience or ability. This is a mistake. The making of indexes is an art in itself, involving more than a comprehensive knowledge of the general subject being covered, and the use of indexes is no less an art. This deserves emphasis. It is true partly because existing indexes vary greatly in kind, thoroughness, and quality. Even in the use of the best subject indexes the user must meet the indexer part way for really good results. Conscious effort to become a good index user will well repay any scientist. Many a day has been spent in the laboratory seeking information by experiment which might have been obtained in a few minutes, or hours at the most, in the library, had the literature search been efficient. Because of the belief that index searching is a neglected art and yet one of much importance, the remainder of my limited time will be devoted to subject indexes—the most useful kind.

What constitutes a good index? The test is to determine whether or not an index will serve as a reliable means for the location, with a minimum of effort, of every bit of information in the source covered which, according to the indexing basis, that source contains. To meet this test an index must be accurate, complete, sufficiently precise in the information supplied, and so planned and arranged as to be convenient to use. Existing indexes fall far short of this ideal in many cases, and of course somewhat short of it in all cases.

The main purpose in indexing is sometimes partially lost sight of through an effort to bring some sort of classification into it. Classification in connection with indexing frequently detracts from, rather than enhances, the efficiency and usefulness of an index, and is beside the main purpose.

HOW TO USE AN INDEX

The first step in learning how to use subject indexes with maximum effectiveness is to become familiar with the characteristics and peculiarities of important existing chemical indexes. The most significant point to note is whether or not a so-called subject index is really an index of subjects or an index of words. The tendency to index words instead of thoroughly to enter subjects constitutes the greatest weakness in the literature of chemistry. There is a vast difference. Words are of course necessary

in the make-up of a subject index, but it is important for an indexer to remember that the words used in the text of a publication are not necessarily the words suitable for index headings or even modifying phrases. Word indexing leads to omissions, scattering, and unnecessary entries. After the most suitable word or group of words from the indexing point of view has been chosen for a heading, it should of course be used consistently no matter what the wording of the text may be. To illustrate a kind of scattering of entries which may result from word indexing, let us consider such a series of article titles as follows:

"An Apparatus for the Determination of Carbon Dioxide," "A New Absorption Apparatus," "Apparatus for Use in the Analysis of Baking Powder," "An Improved Potash Bulb" and "Flue Gas Analysis." Word indexes would no doubt contain an entry under the heading "Carbon dioxide" for the first title, one under "Absorption apparatus" for the second, under "Baking powder" for the third, under "Potash bulb" for the fourth, and one under "Flue gas" for the fifth, and probably no others. These entries seem reasonable enough if the titles are considered separately without thought of the others. And yet the articles may all be descriptive of the same sort of apparatus. As a matter of fact, all these titles might conceivably be used for the same article; if the author happened to be working on baking powder or on flue gas analysis when he conceived the idea for his novel piece of apparatus, or had it in mind particularly for one purpose or the other, he might choose one of the more specific titles for his article rather than one of the more general ones.

In an index entirely based on subjects rather than words, it would be the task of the indexer to see that all these articles get indexed under one heading, or under each of more than one heading, best with cross references pointing from the other possible headings to the one or more headings used. Or, if there seems to be some justification for scattering owing to differences in point of view (word indexing cannot be gotten away from entirely), he would make sure that the necessary cross references are supplied to lead the index user about from heading to heading so that all entries can be readily located. It is not hard to determine whether or not an index is a word index; when this is suspected or noted, one should look around pretty thoroughly in its use instead of being satisfied that the entries found under the obvious heading are all that the index contains on a subject.

It is important to note the approximate degree of completeness of an index in use. There is perhaps no definite point at which a subject index may be said to be complete. The indexing basis is too indefinite. A great many subject indexes are not as full as they ought to be. Aside from word indexing the indexing merely of titles is the most common reason for incompleteness. Titles cannot be depended upon to furnish the information necessary for adequate subject indexing. An index may be reasonably complete from one point of view and not from others. For example, a publication devoted to bacteriology may not reasonably be expected to be indexed fully from the chemical point of view. Completeness in the information supplied in modifying phrases, as well as completeness in index headings, needs to be taken into consideration. It is necessary, of course, to call forth one's resourcefulness to a special degree if a relatively incomplete index is to be used.

Cross references play an important role in subject indexing and in the use of subject indexes. Word indexing is really hard to avoid and cross references are the great preventive. It is a good sign if a subject index has a plentiful supply of cross references, both on the "see" kind and the "see also" kind.² They make for uniformity and proper correlation. "See also" cross

² Cross references which refer from a possible heading under which no page references are given to the chosen heading where they may be found are called "see" references, as "Mineral oils. See Petroleum;" those which connect headings representing allied subjects or containing related entries are called "see also" references, as "Iron alloys. See also Steel."



GROUP OF OHIO STATE UNIVERSITY CHEMISTS WHO ATTENDED THE PITTSBURGH MEETING

references are of just as much importance as the "see" kind though not as much used. The service which they render in directing the index user to related headings or to headings which, though dissimilar for the most part, have entries under them likely to be of interest to the investigator who refers to the original heading, is often the chief means of making a search complete. It is not reasonable to expect an index user, or an indexer, as a matter of fact, to think of all of the headings representing related or significant subjects under which headings he may find valuable references that might otherwise be missed. Nevertheless, in the careful indexing year after year of a periodical devoted to a more or less definite field, as an abstract journal for example, subjects are come upon in such a variety of connections and from so many angles that it is possible for a truly comprehensive list of cross references to be built up. The suitability of a given "see also" cross reference may not be clear, much less suggest itself, until a specific case in which it is helpful is observed. It often pays to follow up such a cross reference even when it does not look as if it applies in a given case. The indexer, in surveying the whole field year after year, is in a position to make valuable suggestions in the form of cross references calculated to lead the index user from place to place in the index, so that the chances that his search will be really exhaustive as far as that particular index is concerned are much increased.

Persistence is a good qualification for index searching. It is desirable to avoid being too soon satisfied. There is no task in which thoroughness is more important. It involves first a knowledge of the indexing system and of the characteristics of the index. Then one needs to be resourceful, exhausting all possibilities, if he is to avoid some futile searches or incomplete findings. One's fund of general knowledge can usually be brought into service to good advantage.

On account of the necessity of drawing on one's general knowledge in making a literature search in any field, it is in many instances important that one should make his own searches. It is not always safe to let some one less well informed in a certain field make an index search when a complete survey is de-

sired, even though his familiarity with indexes and the literature in general may be better than one's own. Just as some tasks in the laboratory can be turned over to another to advantage, but not the more important determinations and experiments, so some tasks in the library can be delegated to an assistant, but not all such tasks. Knowledge, skill, and power of observation, are factors fruitful of important results in the library as well as in the laboratory. Literature searching is a dignified pursuit, and it cannot with impunity be assigned to a lower level than that of the laboratory side of problems, as far as the attention it receives is concerned.

With a given problem at hand the first step, of course, is to think out the most likely places to look in the indexes to be used. This may be a simple matter or it may be a very difficult one, depending on the nature of the problem. Difficulty increases with indefiniteness. Experience is necessary. In fact, the beginner is often completely at a loss to know what to do at this very first stage of his search. This point is stressed in the Report of the Subcommittee on Research in Chemical Laboratories, presented to the Committee of One Hundred on Scientific Research, New York, December 26, 1916.³ In this report, which commends and recommends courses in chemical literature searching in the universities, it is pointed out that the average graduate "fails to analyze the subject" in which he is interested "into its factors, and hence generally looks for topics which are too general. Because he does not find any references to the problem as a whole as he has it in mind, he assumes that nothing has been done upon it and that there is nothing in the literature which will be of aid to him in the investigation. Were he to separate his subject into its essential parts and then to consult the literature on each factor, he would find considerable information which he otherwise would miss." Even though some index headings to which to turn, perhaps the more important ones, may be brought to mind without ingenuity, the completeness of a search may be marred by a failure properly to analyze the problem. Indexes with cross references, particularly "see also" ones, help.

³ *Science*, 45 (1917), 34.

Too much dependence on cross references is not advisable. They may not be available at all and they are never complete. With a given heading in mind it is well to cudgel one's brain for synonymous words or phrases to try, as well as for variously related subjects, and it is advisable to try these even though entries as expected are found in the first place to which one has turned. Words or phrases with an opposite meaning to the one in mind may serve as subject headings under which desired entries may be found. For example, the searcher interested in viscosity may find significant entries under the heading "Fluidity" in addition to those under "Viscosity." Incidentally, it may be noted that the word "consistency" may serve as a heading for still other related entries. Or, some entries under "Electric resistance" may interest the searcher whose thought on turning to an index was of "Electric conductivity." If such related subjects are not suggested by cross references and have not been thought of in advance, they may be suggested by the nature of some entry under the heading first turned to if one is on the look-out for them.

The resourcefulness required in making a thorough search through subject indexes can best be discussed by treating of an example:

Suppose one were interested in looking up all possible references on vitamins. The first place to which to turn naturally would be the heading "Vitamins" in the indexes to the various reference sources to be used. This would rarely, if ever, be far enough to go. If only one of the indexes contained "see also" cross references, these might be helpful in the use of the other indexes. This playing of one index against another, so to speak, is always a possible means of helping out. Cross references should be looked for. Since it is not always possible to find such cross references and it is not safe to depend too much on them, to be complete one might follow out a line of thought as follows. Vitamins are constituents of foods. It may be worth while to look under "Foods." Entries may be found there with some such a modifying phrase as "accessory constituents of." Vitamins are a factor in health and the effect of foods on health involves the idea of diet or ration. These headings, or this heading if they are combined under "Diet," for example, as would seem best in a true subject index, would no doubt prove fruitful of significant references. Studies of proper diet or of adequate ration for an army would beyond doubt involve the vitamin theory. Experiments to determine the nutritional value of foods are frequently called feeding experiments, so a heading "Feeding experiments" may be looked for to advantage. Food is taken for the purpose of nutrition and the vitamin problem is a nutrition problem. Therefore, the general subject "Nutrition" needs to be examined in the indexes. There is, of course, such a thing as plant nutrition as well as animal nutrition. One might seek to determine, if he did not know, whether or not there is a theory of plant nutrition analogous to the vitamin theory in animal nutrition, so the heading "Plant nutrition" or the heading "Plants" would be suggested. If he did not know it, he would likely learn that there are substances supposed to be factors in plant life, called *auxinones* by Bottomley, which are analogous to the vitamins in animal nutrition. The heading "Auxinones" would, of course, then be suggested for reference. The lack of vitamins in the diet is considered by some to be the cause of certain diseases (beriberi, pellagra, polyneuritis, scurvy, xerophthalmia). These ought, therefore, to be referred to as index headings. The general heading "Diseases" should be tried also, such a modifying word as "deficiency" being looked for. Perhaps the next thing for the index user to do would be to ask himself, or someone else, whether or not there is a definite name for this general type of disease; he would find that there is and that the name is *avitaminosis*, which should then be turned to as a heading. Certain specific foods have been used and studied, particularly with reference to the vitamin theory—as, for example, polished rice, milk, butter, orange juice, yeast, tomatoes, etc. It seems unreasonable to be expected to think of these, or at least all of them and yet an article entitled, say, "The Effect on Pigeons of Eating Polished Rice," may be word-indexed only in some index, and therefore only get under the headings "Rice" and perhaps "Pigeons." Vitamins have been differentiated as "fat-soluble A," "water-soluble B," etc., and are sometimes spoken of merely in these ways. It is conceivable that some indexes may have these names as headings. In the earlier literature studies resembling the modern vitamin studies are to be found in which other names for the accessory food constituents are

used, as nutramines (Abderhalden), bios (Wildiers) and oryzanin (Suzuki). The text referred to from any one of the above-mentioned headings may suggest still other headings, as the names of specific foods supposed to be rich in vitamins.

The principle of referring to the general as well as to the specific subject, as exemplified in the preceding paragraph by the subject "avitaminosis" for the general and by the individual deficiency diseases (beriberi, etc.) for the specific, is a good one to keep constantly in mind in using subject indexes. This principle applies aptly in searches for information regarding compounds. Group names for compounds may serve as index headings under which entries of interest to the searcher interested in an individual compound may be found. An example will serve to illustrate:

Supposing one were interested in finding all the information he could with reference to the electrolysis of sodium chloride. In addition to looking up the references under the heading "Sodium chloride" in the indexes to be used, it would be desirable to look also for entries of interest under such headings as the following: "Alkali metal halides," "Chlorides," and "Halides." A process described for the electrolysis of alkali metal halides in general may be of just as much interest and value to the search in hand as one specified to be particularly for sodium chloride, and yet the indexes are not likely to carry entries for each of the members of a group of compounds if a definite group is under discussion. Cross references may be supplied in some cases but it is hardly reasonable to expect an index to go further. A process for electrolyzing chlorides, for instance, could not within reason be entered under headings representing each of the numerous known chlorides. The index user must expect to think of such possibilities and make his search complete accordingly. Another different kind of lead to follow to insure a complete search, particularly when the indexes to be used are word indexes, is to think of the products of the process being studied, in this case chlorine, sodium hydroxide, and possibly sodium hypochlorite. And in addition to looking up the headings represented by the names of these compounds, completeness is insured only by trying the headings "Halogens," "Alkalies," or "Alkali metal hydroxides," and again possibly "Alkali metal hypohalites" and "Hypohalites." The product of some simple electrolytic process which does not involve the recovery of chlorine or alkali may be merely called "bleaching solution" or be given some like name. And still further it may be worth while to look up such a heading as "Potassium chloride" as a representative of a closely related compound which might be subjected to a similar process, or at least might be studied as to the possibilities. Still other headings worthy to be tried are "Electrolytic cells" and possibly "Electrolysis;" this last heading, however, is too general to be used as an index heading for every process involving electrolysis, and is not likely to be used for studies or discussions of specific substances. This whole example serves to show again that resourcefulness and the use of one's general knowledge of chemistry must come prominently into play in the making of index searches.

The resourcefulness necessary in the location of information by means of the great variety of subject indexes in existence may seem to be little more than clever guessing at times. A paper on glass, so called and indexed only under "Glass," may reveal a principle governing the action of metals or other under-cooled melts. Authors often fail to see the full significance of their experimental results, and it is not often that the indexer will go further than the author in bringing out this significance for attention. The kind of flexible ingenuity necessary for the location of information in this way is perhaps only to be acquired by experience. It is really more than guessing that results in the location of information in this way, and yet it seems as if a little more than reasoning power, something like intuition, is sometimes necessary.

Chemical publications present a special problem, both to the subject indexer and to the index user, in that many headings must consist of the names of chemical compounds. The difficulties encountered are to be attributed (1) to the fact that many compounds have, or may have, more than one name, (2) the names, or at least the best names, of the more complex compounds may be difficult to ascertain, and (3) new compounds are constantly being prepared, which, if named at all, may receive more

than one name which is justified from one point of view or another, and the possibilities of incorrect names are great.

It is not feasible to enter into a detailed discussion of the best procedure in building or using indexes of chemical compounds. The difficulties increase with increasing complexity of compounds. Some indexes are based on systematic nomenclature, irrespective of names used by authors; others are not. Cross references within an index and introductions thereto, and the use by index searchers of dictionaries, chemical encyclopedias, handbooks, and other sources of information leading to a knowledge of the names, sometimes numerous, of compounds, are helps to be utilized. As mentioned above, a knowledge of what constitutes good nomenclature is a great aid in the location of compounds in name indexes. This is particularly important for the organic chemist. It is on account of the almost insurmountable difficulties due to the complexities of chemical nomenclature and because of language differences, that a basis other than their names—namely, their empirical formulas—has been sought and, to a limited extent, used, in the indexing of compounds. A formula index provides a certain means for the location of individual compounds; it is very doubtful if the average chemist can locate compounds in all cases in name indexes even though systematic nomenclature may have been consistently followed in the indexing. In name indexes it is possible, by appropriate devices, to group related

compounds to good advantage. This is well brought out in a discussion written in 1919 by Dr. Austin M. Patterson.⁴

The subject index searcher is confronted with nomenclature problems relating to fields other than that of chemical compounds. For example, the chemist interested in plants must contend with the fact that some indexes use the scientific names (genus and species) of plants as headings and others use common names, of which there are frequently several for the same plant.

The use of indexes in foreign languages presents obvious difficulties. It is one thing to be able to read a foreign language and another to translate one's thoughts into that language. The use of an English-French, English-German, or other like dictionary, depending on the language involved, is about the only help available. The introduction to Patterson's German-English Dictionary for Chemists and that to his French-English Dictionary contain some helpful suggestions useful for determining German and French names of chemical compounds.

May I conclude by asking a question? Of the limited amount of information which we as individuals can store in our heads, is it not preëminently desirable that a part of that information consist of a thorough knowledge of where and how to locate additional information when needed?

⁴ THIS JOURNAL, 11 (1919), 989.

Research: Its Position in the Making of an Industry

By John E. Teeple

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FOR THE last three or four years I have been very much interested in three different problems, all in industrial chemistry but in widely separated fields: (1) manufacture of decolorizing carbon, (2) cracking heavy petroleum, (3) manufacture of potash. Although in such widely separated fields, there was a close similarity in the method of handling each one. The ultimate aim in each case was to build a stable industry.

DECOLORIZING CARBON

In this case the starting point was a process brought to me for investigation. The process proved entirely impractical. The next step was to accumulate some organized facts regarding the importance of various factors in making a good decolorizing carbon, factors such as temperature, pressure, time, raw material, catalyzers, state of division, reaction with gases. On the basis of the facts so gathered, I propounded a working hypothesis to guide the further investigation. The hypothesis was probably wrong in whole or in part, but it served its purpose in directing the work.

We finally succeeded in making on a small scale in the laboratory a better carbon than any commercial product that we could find. The study continued in larger apparatus until the laboratory limit was reached. Then came semiplant scale work, then larger units till the full plant-size unit was reached. Finally, these full-sized units were operated for over a year under most widely varying conditions, until we knew, not only the most favorable methods of operation and treatment on a large scale, but also the proper materials of construction, the shape, size, type, and life of equipment, the allowable limits of control, the proper specifications for a marketable decolorizing carbon, and the proper treatment to meet these specifications. Not until then was a plant finally designed and constructed.

You recognize the method: a persistent study of all factors at each step in increasing the size of the operation, from the small-

est laboratory trials to the completed plant. It is slow, but is a very sure way to success. In this case the time was five years from the original discarded impractical process to the full-sized plant, but to-day a plant of over 20 tons per day capacity is in operation making the decolorizing carbon which you know as Darco. This is all that the American industries are educated to using to-day. As their education improves, they will use more, and more plants will be built. This is, in brief, the history of Darco decolorizing carbon from a process which contained no single correct idea to much the largest industry of its kind in America.

CRACKING HEAVY PETROLEUM PRODUCTS

The second problem of cracking heavy petroleum products came to me over four years ago. This was also a process that had passed the laboratory stage, if it ever had one, and was already on a semiplant scale when I first saw it. We succeeded in getting it to operate very, very feebly, so feebly that one had to look twice to be sure it was going, but it seemed to me, after considerable study, to have a basic idea that was right and was possible of commercial development. Having determined this, the next step was to scrap the semicommercial plant and put the operation back into the laboratory to study fundamentals of pressure, temperature, time, character of materials, etc., which should have been done in the first place. From there on its course was the same as the decolorizing carbon. Having learned the respective importance of various factors, it proceeded step by step through the semicommercial-sized unit capable of handling 50 or 60 bbls. per day. To-day it is just going into the last stage of a full-sized unit, and is still probably a year from the design and construction of a full-sized plant. This is the method of cracking oils by using a submerged carbon electrode. It has already been over four years since the process with a right idea in it first came to me for investigation, and in about another year it should be in successful commercial operation.

You recognize the same method as before: A slow and steady trip through the laboratory and semicommercial plants, through full-sized units to the finished industry. Five years in each case. Very slow but very sure.

Now there are many operations that go from an idea to plant practice in much less time, but when it comes to building a new industry or an industry on a new idea it pays to go slow and be thorough and count the time by years—not by days.

This slow progress is usually very aggravating to the inventors and to the people furnishing the money, but I believe it is our duty who are directing such operations to prepare their minds for the long wait, to keep up their interest by intelligent statements of progress, not to allow ourselves to be hurried in any case where results may be prejudiced, and to make them stick to the end. If the people who intend to start such industries have not both the money and the patience to stay by them to the finish, we chemists should discourage them from ever starting.

MANUFACTURE OF POTASH

The third problem was the manufacture of potash. This came to me something over three years ago as a going plant which was using one process and had a dozen more that had been suggested or partially tried out. But, unfortunately, the process was not turning out very pure or high-grade potash, and the plant was losing money every day. After some study, it seemed to me that there was a fair chance of making an industry here, by following the only method I know—that is, first study the fundamentals in the laboratory. A second problem in this case was by proper engineering and management to make the existing plant operate, if possible—but we are not concerned with that to-day. Our problem here is to approach through the research side.

Now these three problems of decolorizing carbon, cracking petroleum, and making potash, have all been developed, you will see, along exactly the same lines, and through the same method, probably because it is the only method I know by which to make a new chemical industry where one did not exist before. The three problems have taken a large part of my time and attention for three or four years. Two of them are now industries and the third is nearly there, but please do not misunderstand me. I did not make these industries. I am not presenting them here as things that I have done. There was a time when a man could know all science that was known, and there was another time when a man could know all chemistry that was known, and there probably was a time when *one* man could make an industry. But now, "Them days is gone forever." Making an industry to-day is a many-man job. It requires the coöperation of many minds of different types and training—the research man, the development man, the engineers, the plant managers, control men, business managers, sales managers, financial managers, and money. If any of these are lacking, the industry either is never born or it dies in early infancy. I cannot stress this point too strongly, because I so often meet the chemist who has an idea or a process and who accordingly thinks that he has a whole industry excepting a few minor details. They are not minor details. Often every one of them is more important than his contribution of an idea or a process.

The credit for making industries like these three I have cited must go to the research, development, and control chemists, the engineers, managers, business, financial and sales directors, and the lawyers, who actually do the work. An adviser like myself deserves credit for only three things: first, for the vision to see that an industry is possible; second, for the common sense to see the logical way to develop it and to get the right men working at the right jobs; and third, for the persistence, some might call it obstinacy, that keeps him sticking firmly and unwaveringly to his course and makes him keep everybody else sticking too. He is often a nuisance, but is necessary.

To come back to our potash industry. Then, according to

formula, the first job was to throw the whole problem back into the laboratory and gather some fundamental information so that we could know what we were doing in the plant, what we could do, and what we could not do. This should all have been done years before, but never had been.¹

The plant now has a capacity of 100 tons of potassium chloride a day and about 50 tons of borax. It has not yet quite reached its production in practice, its best output so far being 93 tons of 97 per cent potassium chloride.

It may seem that we jumped from research laboratory to plant practice at 100 tons per day. But not so. In some cases we did actually so jump because the plant was there, was going in bad shape, and if the jump failed no serious damage was done. But I do not recommend building a plant first and experimenting in it afterward. It is altogether too expensive. More often in my hurried sketch I have simply skipped for your benefit the intermediate struggles.

What I have aimed to do here is to emphasize what I believe is the only safe formula for developing an industry—the slow method of fundamentals—and to show you how this has worked out in the potash industry, showing you only the first steps in the research laboratory and the last step in the plant.

Now before I leave this subject, just a word about organization. This plant is in the desert with no civilization near it except of its own making. The company owns the plant, the town, the stores, pipe lines, water lines, railroad, and its part of the lake. The plant manager is a little czar from whom there can ordinarily be no appeal. Sewage, sanitation, housing, feeding, schools, churches, amusements, health, jealousy among wives of employees and small-town scandals, all come to him as the court of last resort. Chemical problems probably occupy the least of his time. Still I tried hard to find a chemically trained man for the position. Of the many men I considered, some I thought would not do for lack of experience or from improper temperament. Of the few who, I thought, might do, some feared to take a chance on the outcome of the proposition, some hesitated to leave present fairly satisfactory positions, some did not want to take their families to the desert, and some simply did not have the nerve or the insides to tackle the job. I finally quit looking for a chemical man and picked a mining engineer from the Michigan School of Mines, not for his training but for his sane judgment and executive ability developed during many years in mining camps in charge of men. Experience cannot be acquired in college or from books. It must be earned. I think we are making a chemist out of him. For plant superintendent the same thing can be said regarding the type of man wanted and failure to find him among chemical men. I finally took a mechanical engineer—a Cornell man with much executive experience. For director of development and research a chemical man had to be found. The man selected is a Columbia chemical engineer. He was chosen not so much because of his actual research ability but on account of his excellence in development work and his executive ability. This man knows the technical operation of the plant better than any of us—a man who can at any time take charge of the plant at a minute's notice and run it for weeks or months.

This is as strictly a chemical plant as there is in America, having no other production than two chemicals. It may seem strange that the best men found for the positions in a chemical plant should be a mining engineer for the manager, a mechanical engineer for superintendent, and a chemical engineer for the head of the research department. Yet the selections have been happy ones, and the results indicate how much more important personality and experience are than training as soon as a man steps outside of the laboratory or has control in any way of other men.

¹ At this point the author introduced lantern slides illustrating the complexity of the problems encountered and the data incident to their solution. This material will appear later under the authorship of Mr. Harald de Ropp and Mr. W. E. Burke, who did the work.

EIGHTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

Disappointment at the fact that many large, strictly chemical exhibitors have withdrawn in favor of more and more makers of machinery, and speculations as to the future of the Exposition, following a well-defined movement for coöperative management, were the dominant notes in expressions of opinion from visitors at the Eighth National Exposition of Chemical Industries, in the Grand Central Palace, New York, during the week of September 11. Some four hundred exhibitors, largely made up of those who had something to sell the chemical manufacturers, retained for the Exposition its national character, but the absence of many of the chemical exhibitors of previous years was felt by many to have partially nullified its chemical aspect. Meetings of societies and associations in the chemical field, as well as an interesting assortment of addresses and moving pictures dealing with related subjects, added greatly to the interest of the 128,375 visitors in attendance.

The absence of chemical exhibitors lent weight to efforts to revise the plan of the Exposition by making it coöperative. Those fostering this plan believe it possible to bring them into an exposition so operated, and have taken steps to hold a competitive exposition next year on this basis. Just what the outcome will be is difficult to surmise at present, but unquestionably there are a great many supporters for both the present management and the new plan. There are also many exhibitors, however, who incline to the belief that a definite break resulting in two expositions will render both unprofitable from the exhibitors' point of view, and these are planning to await some decision of this point before taking a definite stand on the question. The present management, immediately following the close of the Exposition, stated that in spite of the division the number of contracts already signed for space with them for next year was fully equal to that of previous years.

The exhibits were well arranged and very few failed to show progress in their lines since the previous Exposition. Interest both for technical visitors and for those not acquainted with the details of the industry was held to the fullest extent. Great credit is due those who arranged exhibits for the generally tasteful appearance of the Exposition.

The doors of the Exposition were opened at two o'clock, September 11, by Dr. Chas. H. Herty, president of the Synthetic Organic Chemical Manufacturers Association, and as chairman of the Exposition Committee he presided at the official opening meeting at eight o'clock. Wide interest attached to the address of Wayne B. Wheeler, counsel for the Anti-Saloon League, on the "Attitude of the Anti-Saloon League toward Industrial Alcohol." Other speakers at this session were the Hon. J. M. Wainwright, Acting Secretary of War, Miss Lida Hafford, of the General Federation of Women's Clubs, and Frank H. Riddle, president of the American Ceramic Society.

The Synthetic Organic Chemical Manufacturers Association of the United States met on Tuesday afternoon. The meeting in the conference room on Tuesday evening was addressed by Senator Ransdell, of Louisiana, and Brigadier General Amos A. Fries, of the Chemical Warfare Service. The second annual banquet of the Salesmen's Association of the American Chemical Industry, held Tuesday evening, was addressed by Herbert Hoover, Secretary of Commerce, and by Francis H. Sisson, of the Guaranty Trust Company.

Wednesday was designated as Pulp and Paper Day, and was notable for the session of the Technical Association of the Pulp and Paper Industry, at which representatives of various exhibitors detailed the application of their products to the pulp and paper industry.

Thursday was devoted to the meeting of the Technical Photographic and Microscopical Society, at which the application of photography to technical purposes formed the general subject of a number of informative papers.

The American Ceramic Society met on Friday afternoon, and the New York Section of the American Chemical Society fostered a program on Friday evening which was devoted to standardization in the chemical industry. Notable among the speakers at this meeting was William A. Durgin, of the Department of Commerce, who outlined the accomplishments of the department in the matter of standardization in a wide variety of products and industries in which it has been interested; and Ross C. Purdy, secretary of the American Ceramic Society, who pointed out the virtual impossibility of standardizing refractories on account of the wide variety of uses to which they are put.

On Saturday evening, September 16, at a meeting of the men who went to Washington on August 16 to urge the dye embargo, it was decided to continue for the time being as a loosely knit organization, and to request each plant in the synthetic organic field to appoint a representative to keep in touch with Mr. Pastene, who will maintain touch with the Synthetic Organic Chemical Manufacturers Association, in order that the chemists in these plants shall be kept informed of conditions in their industry and be ready to act on occasion. The suggestion was also made that the AMERICAN CHEMICAL SOCIETY be asked to appoint, through its local sections, men whose duty it shall be to interview and inform each newly elected congressman from that particular territory of the needs and extent of the chemical industry within his district.

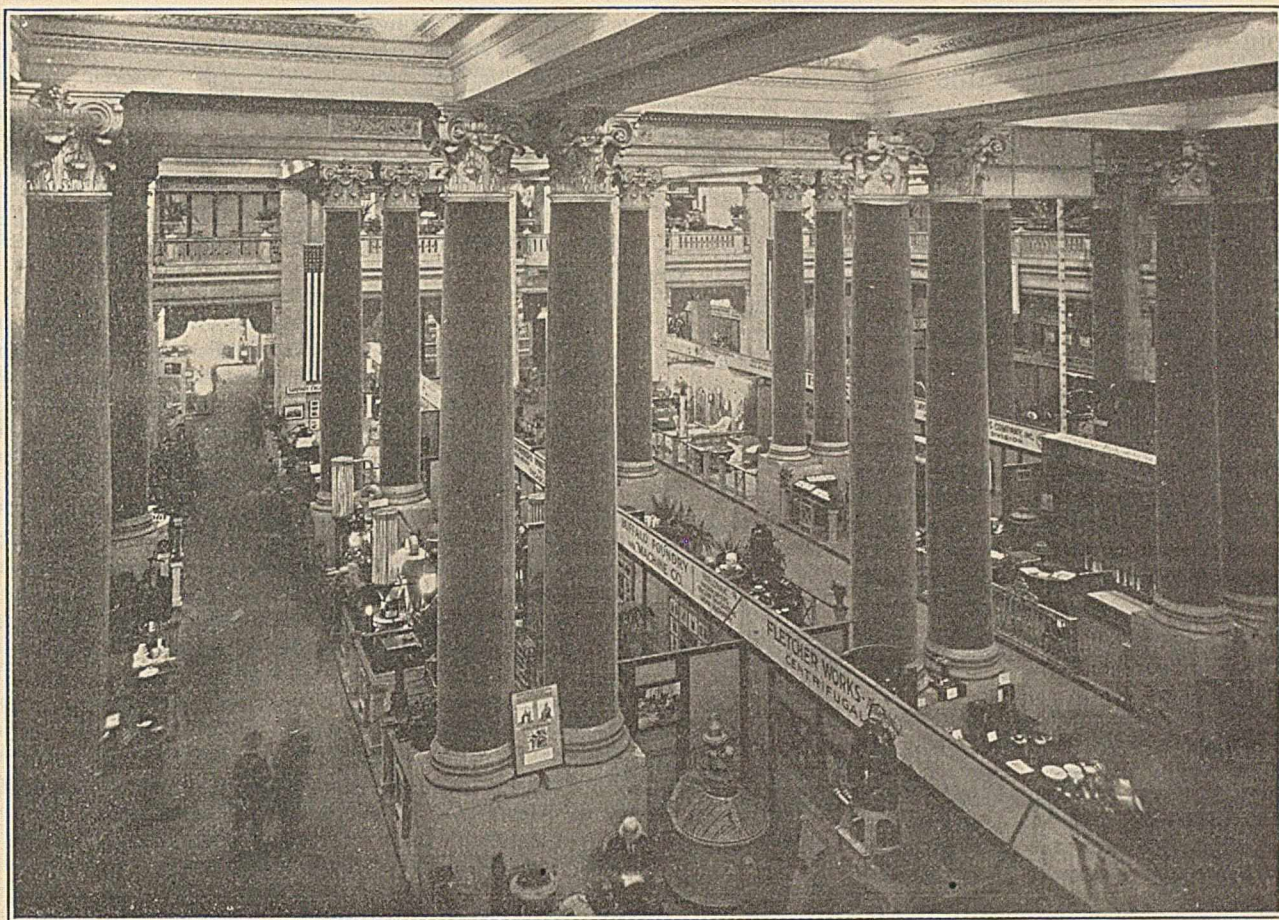
Throughout the week, moving pictures dealing with a wide variety of subjects interesting to visitors were shown in a room especially provided for the purpose.

But to return to the exhibits. Probably the most striking feature of these was the absence of four of the five companies, forming the Allied Chemical & Dye Corporation, whose very picturesque booths were the outstanding feature of last year's show. The Barrett Company, occupying a comparatively small and inconspicuous booth, was the sole representative of this group. The du Pont companies were nowhere represented, even by chairs as last year. The Dow Chemical Company and the Sherwin-Williams Company failed to exhibit. These were conspicuous among the absentees.

As last year, the glass blower at the Corning Glass Company booth was a center of attraction. This year he was rivaled by the potter at his wheel in the General Ceramics Company display on the ground floor, who got at the visitors first.

The zinc and copper companies vied with each other in drawing attention to the superior values of their materials for roofing, but at the close of the show no decision was reached.

Of the dye companies only two had exhibits of real interest. Bachmeier & Company had some remarkable specimens of



batik work and artificial flowers. Zinsser & Company presented highly decorative specimens of alizarin print goods and of heavy woollens and hat blanks. The Newport Chemical Works went no farther than decorating a booth in bright colors.

For the first time the U. S. Department of Commerce exhibited, with the idea of drawing attention to its new chemical division and its services to the industry. The Bureau of Chemistry and the Bureau of Mines were both represented.

One of the most interesting exhibits in the entire show was that of the Technical Photographic and Microscopic Society, showing the application of photography—microscopic, color, airplane and motion picture—to technical operations. The airplane map of the City of New York attracted special attention. In this connection the display of optical instruments by the Bausch & Lomb Optical Company was interesting.

It was indeed surprising to find the press room occupying double booth space on the first floor as it was to find the AMERICAN CHEMICAL SOCIETY occupying that generally considered the du Pont space.

The Exposition was well advertised in New York. Even the Fifth Avenue buses carried signs bearing the legend, "Welcome Chemists."

A Yale Idea

At the Sixth Exposition, the Sheffield Scientific School of Yale University initiated an experiment, under the direction of Prof. T. B. Johnson and in the immediate charge of Prof. W. T. Read. The juniors in industrial and engineer-

ing chemistry were taken to the Exposition to spend the entire week, attending lectures in the morning and devoting the afternoons to visits at the various booths to study apparatus and machinery used in chemical industry. Upon returning to New Haven the class was given an examination. In the opinion of the Yale authorities, the experiment was so successful that it has been repeated every year since 1920. The students have gained a conception of the construction and operation of chemical apparatus, and have been infinitely benefited by the revelation of the vast scope and power of the chemical industry. The inspiration and vision obtained could not have been gained in any other way.

The success of this plan should encourage other universities and technical schools to make the most of the opportunity which the Exposition affords. There seems to be no reason why small groups from several schools should not combine in providing a very desirable audience, before which the technologists always present at the Exposition could appear and discuss in some detail fundamentals underlying the construction of various types of apparatus to be found in the booths. As Professor Read has suggested, headquarters could be established in a booth devoted to visiting university and college students, where catalogs and trade literature, mounted photographs and drawings, lantern slides and motion picture films, would be found filed under proper classifications so as to be easily accessible. The various exhibits themselves could be cross-indexed in such a way that students might readily find the things they need to see and examine.

A wise choice of experts, whose principal object was instruction rather than sales talk, would give these students a corps of teachers—authorities in their special subjects—which could not be equaled.

Conference on Standardization of Biological Stains

A conference on the standardization of biological stains, at which H. J. Conn presided, was held at the Chemists' Club, New York City, September 16, 1922. The objects of the conference were to arrive at some program whereby the user, the manufacturer and dealer may be benefited. It was the sense of the committee that the user should know when he purchased a stain that it was reliable and for what purposes, and that the stain business be put on a more economical basis, the committee's ability to test stains be placed more directly at the service of the manufacturer, and that plans be formulated for educating the users as to the excellence of American stains and the public as to the importance of this line of business.

The following resolutions were adopted:

(1) That those present lend their support to the continuance of the work of the present committee on standardization.

(2) That, should it be found that the National Research Council does not see its way clear to continue its support, it be recommended that the committee take such independent action as is necessary to carry on its work of standardization and control.

It was further recommended, but without a record vote:

(1) That a list of dyes needed for biological purposes with their Schultz numbers be prepared and that the approximate quantities of each sold be sent to the committee with a view to limiting productive effort to necessary ones only.

(2) That the list of dyes chosen as necessary be published and that standard labels be used on packages in which these dyes are sold.

(3) That these standard labels be given proper publicity by publication.

(4) That the American Society of Bacteriologists arrange for the certification and standardization of such dyes and that they charge a fee for such certification.

More than 90 were present at the dinner of the American Institute of Chemical Engineers at the Pennsylvania Hotel on September 14. It was announced that the Institute now has 550 members and 15 applications. As compared with a \$700 balance in the treasury a year ago, there is now \$2100 on hand, and there are no outstanding bills. David Wesson, H. C. Parmalee, H. C. V. Dorr, and Maximilian Toch, spoke during the meeting, and a committee, composed of David Wesson, G. W. Thompson, and R. F. Bacon, was appointed to consider the repeal of the New York law governing the registration of chemical engineers.

Richmond, Va., will be the place of the December meeting, the tentative dates being December 11, 12, and 13.

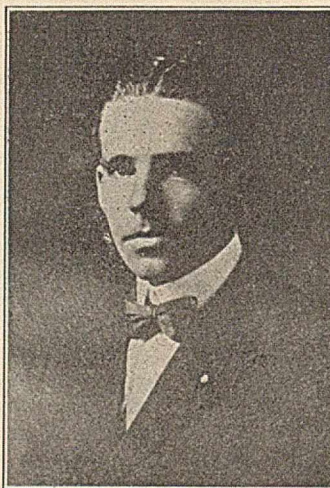
Progress in Inorganic Electrochemistry

By W. G. Horsch

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IN REVIEWING recent progress in inorganic electrochemistry, it seems desirable to include as many topics as possible, touching on each one briefly, and indicating where further information may be found.

The subject of metal recovery will be first considered. Of considerable interest is the well-worked-out Ashcroft process for the electrolytic decomposition of anhydrous magnesium chloride employed by the Magnesium Company of Wolverhampton, England,¹ magnesium being first recovered as an alloy with lead, which is subsequently refined electrolytically. Other methods of magnesium recovery have been patented by Seward² using a fused fluoride bath, and by Ingeberg.³ Its recovery from salt-works residue has also been investigated.⁴ A brief review of magnesium recovery processes is given by Vickers.⁵ Electrolytic zinc apparently has become a permanent industry both in United States and abroad, according to Ingalls,⁶ although it is dependent upon large-scale production. It is advocated as an economic proposition in Great Britain.⁷ Only a few of the many references can be given. Low cobalt content of the electrolyte is impor-



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tant.⁸ One part antimony in two million causes trouble.⁹ Several interesting descriptions of plants have been published: Trail, B. C., with a daily capacity of 75 tons;¹⁰ Judge Electrolytic Zinc Plant;¹¹ and Anacanda.¹² Cadmium is recovered from the bag-house condensation product of copper and lead furnaces, the electrolyte being a pure sulfuric acid leach.¹³ Excellent results are claimed for a new cell for producing metallic calcium.¹⁴ Recent patents cover the electrolytic production of sodium from fused sodium chloride¹⁵ and from sodium carbonate in a fused mixture with sodium chloride.¹⁶ Difficulties due to the high vapor pressure of sodium caused the failure of early attempts to use sodium chloride. Electrolysis of fused boric acid, rendered conductive by adding borax, yields boron, a useful metallurgical reducing agent.¹⁷ Patents continue to be issued

covering processes for the electrolytic detinning of scrap.¹⁸ Cerium and "misch-metal," obtained by electrolyzing residues

⁸ Brit. Patent 126,296 (1919); Clevenger, U. S. Patent 1,283,077.

⁹ Hansen, *Mining Met.*, **157**, Sec. 12 (1920), 21.

¹⁰ *Chem. Met. Eng.*, **23** (1920), 227.

¹¹ Heikes, *Eng. Mining J.*, **110** (1920), 1118.

¹² Laist, et al., *Trans. Am. Inst. Mining Eng.*, **1920**, 1028; *Chem. Met. Eng.*, **25** (1921), 754.

¹³ Hanley, *Chem. Met. Eng.*, **23** (1920), 1257.

¹⁴ Brace, *Trans. Am. Electrochem. Soc.*, **37** (1920), 465.

¹⁵ Weaver, U. S. Patent 1,323,936.

¹⁶ Smith and Veazey, U. S. Patent 1,334,179.

¹⁷ Constant and Raisin, Brit. Patent 162,252.

¹⁸ Brit. Patents 122,618, 154,242, and 170,861.

¹ *Electrician* (London), **88** (1922), 90.

² U. S. Patents 1,408,141-2.

³ Ger. Patent 319,530 (1917).

⁴ Boynton, Langford and Hicks, *THIS JOURNAL*, **14** (1922), 146.

⁵ *Brass World*, **16** (1920), 330.

⁶ *Trans. Am. Electrochem. Soc.*, **40** (1921), 165.

⁷ Field, *Trans. Faraday Soc.*, **17**, II (1922), 400.

from the gas mantle industry, alloyed with iron, produce the pyrophoric alloy used in gas lighters.¹⁹ Other metals that may be deposited electrolytically are chromium,²⁰ molybdenum²¹ and tungsten,²² the last mentioned being a purification process at 1300° C. The electrolytic recovery of iron from the slime produced by treating iron compounds with caustic alkali has been proposed,²³ also its recovery from waste liquors from the reduction of aromatic nitro compounds,²⁴ the principal justification being processes demanding a very pure grade of iron.

Refining, plating, and electrotyping—processes carried out similarly but differing in purpose—will next be considered. The refining of tin was begun at Perth Amboy in 1916,²⁵ using a fluosilicate solution later given up in favor of sulfate. A modified fluosilicate solution was recently patented by Mathers.²⁶ Newman²⁷ describes a process in which sodium sulfide solution is used. Nickel also may be refined electrolytically.²⁸

Electroplating is gradually being removed from a rule-of-thumb to a scientific basis. In the deposition of nickel, Blum²⁹ has shown that deposits of finer structure and higher tensile strength are obtained from fluoride solutions than from the corresponding chloride solutions. Madsen³⁰ achieves a similar result by alternately raising and lowering the cathode. Mazuir³¹ gives a method for nickel-plating aluminium. Dense adherent deposits of tin are obtained from stannous sulfate solutions containing gelatin.³² Pyrophosphate baths also are recommended.³³ A novel use for copper is the plating of wooden airplane propellers.³⁴ Considerable attention has been given lately to zinc plating, which affords better protection than dip galvanizing.³⁵ Cadmium, plated on iron, successfully resists rusting.³⁶ Building up the worn parts of machinery by electro-deposited iron has been found practicable.³⁷ Electrolytic iron has been extensively investigated by Hughes;³⁸ commercial plant design by McMahon.³⁹

In the field of electrotyping, an innovation developed by the Bureau of Standards is the substitution for wax of negatives made by alternately deposited layers of nickel and copper.⁴⁰

Electrolytically formed alloys which have been developed recently are tin-lead⁴¹ and calcium-barium-lead.⁴² The science of brass deposition has been extended.⁴³

In the field of electrochemical production of chemical compounds many processes have been developed. Some of the

following cannot be produced economically under present market conditions, while others are being actively produced on a commercial scale. Anhydrous aluminium chloride,⁴⁴ arsenate of lead,⁴⁵ chromic acid,⁴⁶ ferrieyanide,⁴⁷ hydrogen peroxide,⁴⁸ perborates,⁴⁹ perchlorates,⁵⁰ perchloric acid by oxidation of hydrochloric acid,⁵¹ permanganate.⁵²

Patents are constantly being granted for improvements in the alkali-chlorine industry. These relate mostly to the structural features of cells and diaphragms. A process for recovering bromine from natural brine has been developed.⁵³ The electrolysis of fused potassium acid fluoride is said to be the best and simplest method known for preparing fluorine.⁵⁴ Electrolytic hydrogen and oxygen likewise form a large part of the patent literature. Stimulated by the commercial demand, highly practical cells have been produced.⁵⁵

The phenomenon of cataphoresis has been applied to the purification of clays, to ore concentration, and to the preparation of silica gels from sodium silicate.⁵⁶

Progress has been made in the production of "insoluble" anodes.⁵⁷

Improvements in primary and secondary cells are numerous, but not very striking. A few instances only will be cited. In the indispensable dry cell, the use of porous carbon as a depolarizer has been described.⁵⁸ The old problem of the fuel cell is still being studied. A number of cells were tested at temperatures near 800° by Bauer.⁵⁹ The combustible materials in the various types were coke dust, carbon rods, hydrogen, and illuminating gas. They are said to possess commercial possibilities. Attempts have been made to reduce nitrogen cathodically to ammonia.⁶⁰ The electrolytic fixation of nitrogen as nitric oxide has been patented.⁶¹ A recent development in secondary cells is a very thin plate battery giving much longer life and greater output per unit weight.⁶² The theory of the lead cell has been further investigated.⁶³

In conclusion it may be stated that whereas electrolysis was originally confined chiefly to electroplating and later extended to refining, it is now taking an increasingly important place in the recovery of metals. As a means of producing chemical compounds, it is often useful but the efficiency in many cases is low. The electrochemist needs improved diaphragms and unattackable anodes which will withstand severe conditions. The development of processes in such a manner as to utilize off-peak power⁶⁴ offers many interesting possibilities. The working out of an electrolytic process for iron, using iron ore as a starting point, would be valuable to those localities where iron ore and cheap power are available. The possibilities for research are extensive.

¹⁹ Hirsch, *Trans. Am. Electrochem. Soc.*, **37** (1920). See also *Brass World*, **16** (1920), 89.

²⁰ Sargent, *Trans. Am. Electrochem. Soc.*, **37** (1920); Liebreich, *Brit. Patent* 164,731 (1921).

²¹ Förland, U. S. Patent 1,305,350.

²² Keyes, U. S. Patent 1,293,117.

²³ Estelle, *Can. Patent* 188,462 (1919).

²⁴ Kitsee, U. S. Patent 1,298,513.

²⁵ *Trans. Am. Electrochem. Soc.*, **38** (1920), 163.

²⁶ U. S. Patent 1,397,222 (1921).

²⁷ *Z. Elektrochem.*, **27** (1921), 256.

²⁸ Guess, *Trans. Am. Electrochem. Soc.*, **35** (1919).

²⁹ *Trans. Am. Electrochem. Soc.*, **39** (1921), 227.

³⁰ *Ibid.*, **39** (1921), 269.

³¹ *Ann. chim. anal. chim. appl.*, **2** (1920), 335; *C. A.*, **15** (1921), 989.

³² Schlotter, *Brit. Patent* 148,334 (1920).

³³ Lotterman, *Z. Elektrochem.*, **27** (1922), 573.

³⁴ Merritt, U. S. Patent 1,335,846.

³⁵ Wernlund, *Trans. Am. Electrochem. Soc.*, **40** (1921), 345; Horsch and Fuwa, *Ibid.*, **41** (1922), 211.

³⁶ Knox, *Metal Ind.*, **18** (1920), 556.

³⁷ MacFadyen, *Engineering*, **108** (1919), 827.

³⁸ *Trans. Am. Electrochem. Soc.*, **40** (1921); *Electrician*, **86** (1921), 712; *Chem. Met. Eng.*, **26** (1922), 267.

³⁹ *Chem. Met. Eng.*, **26** (1922), 639.

⁴⁰ Blum, *Trans. Am. Electrochem. Soc.*, **40** (1921), 137.

⁴¹ Blum, *Ibid.*, **40** (1921), 147.

⁴² Cowan, *et al.*, *Chem. Met. Eng.*, **25** (1921), 1181.

⁴³ Ferguson and Sturdevant, *Trans. Am. Electrochem. Soc.*, **38** (1920), 87.

⁴⁴ U. S. Patent 1,343,662.

⁴⁵ Tartar and Grant, *THIS JOURNAL*, **14** (1922), 311.

⁴⁶ McKee and Leo, *Ibid.*, **12** (1920), 16.

⁴⁷ Brown, Henke and Miller, *J. Phys. Chem.*, **24** (1920), 230.

⁴⁸ Skirrow and Stein, *Trans. Am. Electrochem. Soc.*, **38** (1920), 209.

⁴⁹ Alsgaard, *Ibid.*, **40** (1921), 173.

⁵⁰ Williams, *Engineering*, **108** (1919), 827; Knibbs and Palfreeman, *Trans. Faraday Soc.*, June 1920.

⁵¹ Goodwin and Walker, *Chem. Met. Eng.*, **25** (1921), 1093.

⁵² *Chem. Met. Eng.*, **21** (1919), 680; *THIS JOURNAL*, **13** (1921), 763; U. S. Patent 1,377,485.

⁵³ Dow, U. S. Patent 1,376,610.

⁵⁴ Argo, *Trans. Am. Electrochem. Soc.*, **35** (1919), 355; Meyer and Sandow, *Ber.*, **54** (1921), 759.

⁵⁵ Barnitz, *Chem. Met. Eng.*, **22** (1920), 201.

⁵⁶ Ormandy, *Chem. Age (London)*, **3** (1920), 475.

⁵⁷ Fink and Eldridge, *Trans. Am. Electrochem. Soc.*, **40** (1921), 335.

⁵⁸ *Compt. rend.*, **172** (1921), 317.

⁵⁹ *Z. Elektrochem.*, **27** (1921), 199; *C. A.*, **16** (1922), 206.

⁶⁰ Tiede, *Z. Elektrochem.*, **27** (1921), 112.

⁶¹ U. S. Patent 1,376,207.

⁶² Hazlett, *Trans. Am. Electrochem. Soc.*, **39** (1921), 89.

⁶³ MacInnes, *Ibid.*, **37** (1920), 383.

⁶⁴ Benson, *Chem. Met. Eng.*, **25** (1921), 1004.

Progress in Organic Electrochemistry

By E. K. Strachan

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THE ELECTROCHEMICAL manufacturers of this country have not, as a rule, been interested in organic chemicals, except as an outlet for some of their by-products, chief of which have been chlorine and hydrogen. The manufacture of monochlorobenzene has reached the proportions of a real industry, and the production of *p*-dichlorobenzene has been stimulated by the discovery of its insecticidal properties, while benzaldehyde and benzoic acid have cut no small figure. Apparently the chlorination of acetylene has never been carried out on any very large scale. The manufacturers of organic chemicals in several instances have turned to electrochemical methods for the recovery of spent reagents, particularly the chromate used for oxidation processes. More than one fair-sized factory has been established on this basis, and promises to survive considerable competition. However, it is the purpose of this review to set forth recent progress in the study of those processes which consist of reaction on an organic material in the electrolytic cell. Very few such are in operation on a factory scale, but those that are give promise of considerable commercial success both for materials requiring tonnage production, and for the manufacture of small quantities of fine chemicals of high purity. But on the whole, the investigation of organic electrochemical methods has proceeded but little beyond the laboratory research stage.

During the period when acetic acid had to be obtained at any cost whatever, thousands of tons of it were made from calcium carbide through acetylene and acetaldehyde. This method cannot compete with wood distillation under present economic conditions, particularly as the makers of pyroline acid can throw the burden of competition on their methanol.¹ Nevertheless, this war-time development called attention to the great variety of organic chemicals that can be produced from acetylene.² These include aldehyde, paraldehyde, alcohol, acetic acid, ethyl acetate, acetone, ethylene, acetonitrile, pyridine, pyrrole, thiophene, mercaptan, dichloroethane, tetrachloroethane, many other chloro derivatives, chloroacetic acid, crotonic aldehyde, pinacone, isobutyl alcohol, and many other compounds. The shifting of economic conditions and further research may make these reactions of considerable commercial importance: power may be cheaper, motor fuel will undoubtedly increase in price, wood for distillation is apt to be very much scarcer, substitutes or new manufacturing methods may eliminate the strategic importance of methanol. The whole group of materials presents interesting electrochemical possibilities.

Electrochemical methods were applied to this group first for the recovery of the spent mercury catalyst used in the hydration of acetylene. Then it was proposed to make the process continuous by conducting the hydration of the acetylene and recovery of the mercury simultaneously in an elec-

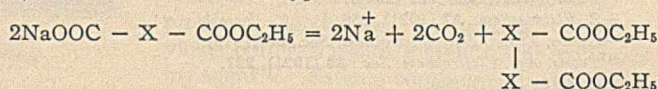
trolytic cell especially devised for the purpose. And finally they were used as an alternative to continue the oxidation until the aldehyde was converted to acetic acid.³ Other investigations have dealt with the electrolytic oxidation of aldehyde or paraldehyde to acid.⁴ Apparently the formation of acid is accelerated by the presence of salts of Mn, Ce, Mo, and V, substances that are known to catalyze other oxidation reactions. The acetic acid may be increased to 40 per cent before it is removed from the electrolyte by distillation. Or, if equivalent alcohol is added before distillation, ethyl acetate is produced.⁵ The conversion of acetic acid to acetone is essentially a thermal process, but the reduction of acetone to pinacone may be performed electrolytically,⁶ and has received more or less attention. It has been found that the ratio of pinacone to isopropyl alcohol is determined by the electrode material; with electrodes of 90 Pb and 10 Sn, the ratio pinacone: isopropyl alcohol is 10:1, while with graphite electrodes the ratio is 6 or 7:1. Furthermore, the presence of salts of Bi, Hg, Mn, Ni, Sb, Ag, and Fe tend to reduce the proportion of isopropyl alcohol.

The production of ethyl alcohol from acetaldehyde has received considerable attention.⁷ It appears that the concentration of aldehyde must be kept low during the process, never exceeding 10 per cent, and preferably less, to avoid the formation of aldehyde condensation products. By altering the conditions of electrolysis, *e. g.*, raising the temperature, or increasing the aldehyde concentration, polymers and their reduction products, such as crotonic aldehyde, butane-1, 3-diol, butyl alcohol, etc., may be formed which can serve as denaturants, and thus a denatured alcohol is produced directly from aldehyde.⁸

The reduction of mixtures of aliphatic aldehydes and ketones to diols is described in Brit. Patent 156,145 (1920).

It is interesting to note that in the complete absence of air, aldehyde may be catalytically reduced to ether, although apparently no one has ever done this electrolytically.⁹

There has been interesting progress in the reduction of ω, ω -dibasic acids.¹⁰ The type reaction



in which X = CH₂ has been repeated until a C₁₈ acid has been prepared from sodium ethyl malonate. The next step, which would result in the formation of a C₃₄ acid, was unsuccessful, probably on account of the soapy and colloidal character of



E. K. STRACHAN

¹ *J. Soc. Chem. Ind.*, 40 (1921), 345R.

² *Chimie et industrie*, 6 (1921), 239; *J. Soc. Chem. Ind.*, 41 (1921), 18R.

³ Brit. Patents 143,891 and 156,147 (1920).

⁴ Brit. Patent 124,195 (1919).

⁵ Brit. Patent 131,600 (1919). For ethyl acetate see also Brit. Patent 140,115 (1918).

⁶ D. R. P. 324,920; 306,304; 324,919 (1917).

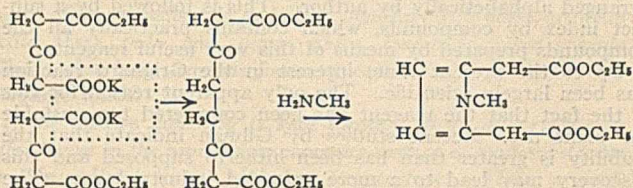
⁷ D. R. P. 328,342; Brit. Patent 140,115 (1918).

⁸ Brit. Patents 140,527 (1919); 140,115 (1918).

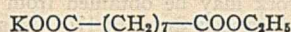
⁹ Brit. Patent 156,145 (1920); D. R. P. 317,589 (1918).

¹⁰ *J. Soc. Chem. Ind.*, 40 (1920), 169R.

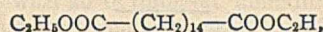
the products. This method has not been applied to aromatic compounds, but work is promised in the near future. The same type of reaction has been proposed as a starting point for the synthesis of tropine derivatives, the basic substances of the atropine, cocaine, and scopolamine groups of alkaloids.¹¹ It affords an excellent example of the use of electrochemical methods for the production of fine chemicals, a field of manufacture for which they are particularly well adapted. The potassium ethyl ester of acetone dicarboxylic acid, which can be prepared from citric acid, is reduced electrolytically and condenses with itself to succinyl diacetic diethyl ester. The latter substance can be condensed with methyl amine to form *N*-methyl pyrrole diacetic diethyl ester, which in turn can be transformed to tropinone.



By the same method, the potassium ethyl ester of azelaic acid

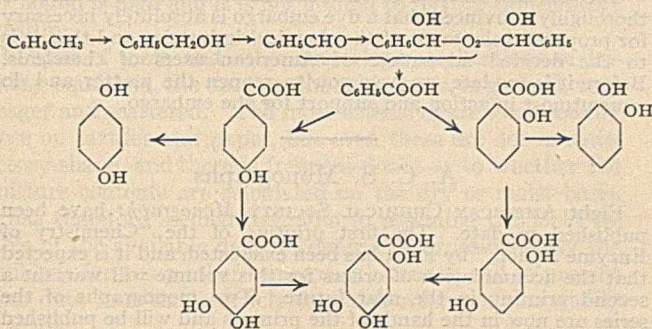


has been converted to



the acid of which proved to be identical with the thapsic acid from juniper berries.¹²

The work of Fichter and his associates deserves especial attention. They have investigated the oxidation of toluene in considerable detail, and find that it proceeds in accordance with the following diagram:¹³



If the various reactions indicated in this diagram can be controlled it suggests interesting possibilities in the production of fine organic chemicals.

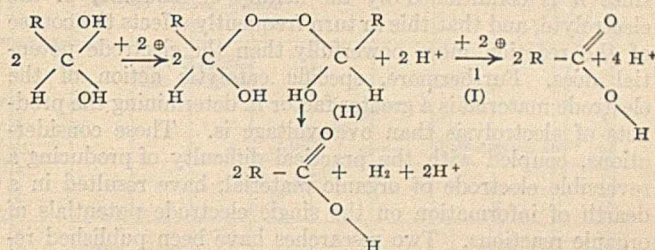
The oxidation of dimethylaniline yields tetramethylbenzidine, which is interesting in view of the fact that the analogous reaction with aniline, in which the amino group is unprotected, has never been observed to yield benzidine.¹⁴ The yield is poor, owing to the formation of CO_2 , N , CO , and CH_2O , the last of which condenses with the amine. Diethylaniline on the contrary yields almost exclusively tetraethylbenzidine.

A series of exploratory studies¹⁵ is in progress in the same laboratory, one of which¹⁶ shows the formation of *p*-aminophenol from azobenzene. The electrolytic oxidation of azobenzene yields *p,p*-dihydroxyazobenzene, and about twice

as much tetrahydroxyazobenzene. This is another illustration of the tendency of organic compounds to oxidize to a greater degree than is desired. Dihydroxyazobenzene of course reduces readily to *p*-aminophenol.

The electrolytic oxidation of naphthalene apparently is similar to that of benzene.¹⁷ Just as the oxidation of benzene does not stop with the formation of phenol or hydroquinone, but proceeds to quinone, so the oxidation of naphthalene yields naphthoquinone as the principal product with traces of α -naphthol, some 1,4-dihydroxynaphthalene, a compound of the quinhydrone type, and phthalic acid.

It was observed sometime ago that, when formaldehyde solution is electrolyzed, equal amounts of hydrogen appear at the anode and cathode for a while, and that then the evolution at the anode gradually ceases. The explanation of this phenomenon constitutes a valuable contribution to the theory of oxidation of aldehydes.¹⁸ The investigator found that by use of a suitable anode constructed of copper coil covered with molten cuprous chloride and reduced electrolytically in alkaline solution the evolution of hydrogen at the anode could be made continuous. The same result is obtained with a similarly constructed silver anode. Moreover, the electrolysis of both acetaldehyde and benzaldehyde exhibits the same phenomenon. The course of the reaction is explained by the following scheme:



The catalytic effect of the electrode causes the intermediate peroxide to decompose by Reaction II with the evolution of hydrogen gas at the anode, while the electrolytic oxidation proceeds by Reaction I. It is quite interesting to compare this with the electrolytic oxidation of methyl and ethyl alcohols which yield, respectively, hydrogen and methane.¹⁹

Some interesting facts have come to light in a study of the effect of adding various salts to the electrolyte to decrease the cathodic reduction during the electrolysis of chloride to chlorate.²⁰ In general it appears that the effect of the electrode depends on the system (electrode material-hydrogen-metal deposited from the added salt). Since only small amounts of salt are added—and indeed small amounts of salt appear to be more effective than larger ones—it is probable that the deposited metal does not entirely cover the cathode but merely forms a network on it. Copper deposited on an iron cathode was found to increase reduction, while iron deposited on a copper cathode decreased the reduction to a very small figure. This is strange, since a plain iron cathode reduces much more chlorate than a copper one. The explanation perhaps lies in the capacity of electrolytic iron to occlude hydrogen. These facts should be suggestive to experimenters who are attempting to control the electrochemical oxidation or reduction of an organic material by selection of a suitable electrode. A great deal more work of this sort is needed.

The electrolytic reduction of a number of azo dyes led the investigators to conclude that the rupture always took place at the azo double bond.²¹ A suitable small electrolytic cell

¹¹ D. R. P. 300,872 (1917).

¹² *Biochem. Z.*, **108** (1920), 75.

¹³ Fichter and Uhl, *Helvetica Chim. Acta*, **3** (1920), 22.

¹⁴ Fichter and Rothenberger, *Ibid.*, **5** (1922), 166.

¹⁵ Fichter and Bonhôte, *Ibid.*, **3** (1920), 395; Fichter, Brändlin and Hallauer, *Ibid.*, **3** (1920), 410; Fichter and Schmidt, *Ibid.*, **3** (1920), 704; Fichter and Grissard, *Ibid.*, **4** (1921), 928.

¹⁶ Fichter and Jaeck, *Ibid.*, **4** (1921) 1000.

¹⁷ *J. Chem. Soc. Japan*, **42** (1921), 38; *J. Chem. Soc.*, **120**, I (1921), 334; *J. Chem. Soc. Japan*, **42** (1921), 559; *J. Chem. Soc.*, **120**, I (1921), 726.

¹⁸ Erich Müller, *Ann.*, **420** (1920), 241.

¹⁹ Erich Müller and A. Miro, *Z. Electrochem.*, **27** (1921), 54.

²⁰ Schlötter, *Ibid.*, **27** (1921), 394.

²¹ *Gazz. chim. ital.*, **50** (1920), 149.

should therefore be very useful to the analyst of azo dyes, since it would enable him to split dyes of unknown composition into their components without the addition of any foreign material.

Fierz and Wiessenbach²² report that the reduction of 1,5- and 1,8-nitronaphthalenesulfonic acids, and 1,3,6,8-nitronaphthalenetrisulfonic acid proceeds quite satisfactorily to the corresponding amines. The dye-makers would do well to consider seriously the use of this method of reduction in the factory, since it has much to commend it for the manufacture of H-acid. On the other hand, the reduction of 1,6- and 1,7-nitronaphthalene sulfonic acids produces principally the corresponding hydroxylamines, which rapidly form tarry substances, a statement that sounds quite plausible to anyone who has ever made Cleve acid.

A. Lowy reports the results of a study of the electrolytic oxidation of leucomalachite green.²³

The role of electrochemistry in the dyeing industry has been discussed by F. Mollwo Perkin.²⁴

The possibility of modifying the oxidizing or reducing power of an electrode by altering its potential, and thus exercising control over the products of electrolysis was emphasized by all the early workers in this field who were apparently unaware that the electrode potential is not easy to control, since it is conditioned by the acidity or alkalinity of the electrolyte, and that this in turn frequently affects the course of the reaction more powerfully than the electrode potential does. Furthermore, specific catalytic action of the electrode material is a greater factor in determining the products of electrolysis than over-voltage is. These considerations, coupled with the practical difficulty of producing a reversible electrode of organic material, have resulted in a dearth of information on the single electrode potentials of organic reactions. Two researches have been published recently on this subject, one establishing the potential of the hydroquinone-quinone electrode²⁵ and the other the oxidizing potential of several anthraquinone-sulfonic acids.²⁶ It is disappointing that the authors of the latter article did not exercise that care in establishing the identity and purity of their materials for which their laboratory is famous.

No strikingly new features are embodied in recent patents of cells for the electrolysis of organic materials. Several call for a porous electrode through which the organic material may be forced. Others seek to eliminate the diaphragm by employing difference of density to keep the anolyte and catholyte apart, or depend on rotating parts and centrifugal force or an immiscible solvent for this purpose. One particularly interesting looking device allows benzene to rise through the electrolyte to the anode, above which it collects in a layer and is pumped back to the bottom of the cell again. Circulation is maintained until the desired degree of oxidation is accomplished.²⁷

The literature on the electrochemistry of organic materials gives the casual reader a sense of a great deal of disorganized effort. Such is partly the case, but in this field, as in many of the newer fields of chemical investigation, a great many exploratory experiments must be performed before investigators can define and limit the problem before them. The exploratory work is by no means complete, yet out of the chaos there arise a few guiding generalizations. These, coupled with the knowledge that here and there through the

country an organic reaction is being conducted electrolytically on a paying commercial scale, lead to a firm optimism that organic electrochemistry will play a very considerable part in the establishment of America's organic chemical industry.

Bibliography of the Grignard Reagent

The National Research Council has recently issued, as Reprint and Circular Series No. 24, a bibliography of the Grignard reagent, entitled "Organomagnesium Compounds in Synthetic Chemistry," by Clarence J. West and Henry Gilman. The first 17 pages comprise a brief discussion of the various types of reaction in which the Grignard reagent may be used. The bibliography proper contains about 1500 references and is arranged alphabetically by author. This is followed by a subject index by compounds, which contains practically all the compounds prepared by means of this very useful reagent.

Up to the present time, interest in the Grignard reaction has been largely scientific. The only apparent reason for this is the fact that the reagent has been considered too unstable for plant use. Recent studies by Gilman indicate that the stability is greater than has been hitherto supposed and this discovery may lead to a more extended industrial use. The wide variety of compounds that can be prepared from this reagent should make it very valuable for the manufacture of research chemicals.

Copies of this work may be obtained from the Publication Division, National Research Council, 1701 Massachusetts Ave., Washington, D. C., for \$1.50.

Chicago Chemists Urge Embargo

When the embargo was up in the Senate, fifteen prominent members of the Chicago Section of the AMERICAN CHEMICAL SOCIETY signed the following resolution, which was sent to the senators from Illinois:

The Chicago Section of the AMERICAN CHEMICAL SOCIETY is thoroughly convinced that a dye embargo is absolutely necessary for proper development of the chemical industries and that it is to the decided advantage of American users of chemicals. Before it is too late, we urge you to reopen the matter and do your utmost in action and support for the embargo.

A. C. S. Monographs

Eight AMERICAN CHEMICAL SOCIETY *Monographs* have been published to date. The first printing of the "Chemistry of Enzyme Action," by Falk, has been exhausted, and it is expected that the accumulation of orders for this volume will warrant a second printing in the near future. Two monographs of the series are now in the hands of the printers and will be published during October, five others are expected to be published during this year, and fifteen are in less advanced stages of preparation. The entire series to date numbers thirty volumes and more will be added from time to time.

Record in Gasoline Production

All previous records for monthly production of gasoline in the United States were broken in July, when 569,711,415 gal. were produced, according to figures compiled by the Bureau of Mines. The increase over July of last year is 150,000,000 gal.

Domestic consumption of gasoline for July was also the largest ever recorded in a single month, amounting to 566,000,000 gal. as compared with 457,000,000 gal. for July of last year. The fact that consumption figures showed a larger increase than the production figures accounts for a reduction of stocks of gasoline for the month, amounting to 52,000,000 gal.

A daily average of 1,593,000 bbl. of oil was run through the stills of 305 refineries reported to the Bureau of Mines as operating during July. This shows an increase of 2.96 per cent in the amount of oil run and a decrease of 5 in the number of operating refineries as compared with June. Plants operating in July ran an average of 89.55 per cent of their daily indicated capacity.

Imports of gasoline for July amounted to 4,840,098 gal., exports were 58,630,402 gal., and shipments to insular possessions were 1,866,789 gal.

²² *Helvetica Chim. Acta*, 3 (1920), 305.

²³ *Trans. Am. Electrochem. Soc.*, 1921 (Preprint).

²⁴ *J. Soc. Dyers Colour.*, 36 (1920), 138.

²⁵ Billmann, *Ann. chim.*, 15 (1921), 109; Sørensen and Linderstrom-Lang, *Ibid.*, 16 (1920), 283.

²⁶ Conant, Kahn, Fieser, and Kurtz, *J. Am. Chem. Soc.*, 44 (1922), 1382.

²⁷ U. S. Patent 1,322,580 (1919).

Humidity Equilibria of Various Common Substances^{1,2}

By Robert E. Wilson³ and Tyler Fuwa

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

The following paper is intended to collect for reference, in a single article, data on the humidity equilibria of various common substances.

The paper first discusses the various types of humidity equilibrium curves. Curves are also given for various substances arranged in groups of related materials, as follows: natural textile fibers, artificial textile fibers, pulp and paper fibers, foodstuffs, other organic colloids, absorbents, various forms of carbon, and finely divided inorganic solids.

If the relative humidity is kept constant, there is surprisingly little change in the equilibrium moisture content of most substances over the ordinary range of indoor temperatures. There is need, however, of further work on the effect of temperature changes in connection with hot air drying.

A KNOWLEDGE of humidity equilibria, or the amount of water which is held by various common substances in contact with air of different humidities, is of very considerable importance from a number of different standpoints. The application of such data to problems involving the drying or humidification of materials is obvious. Again, the physical properties of many substances vary greatly, depending upon their precise moisture content. Proper allowances for gain or loss of moisture are also of great importance in buying and selling textiles, etc., where the value per pound is high and it is not desired to pay for unnecessary moisture.

In spite of these and other important applications of humidity equilibria, the data on the subject are, in general, very meager and scattered. The most extensive are undoubtedly those on textiles and paper, but even these are not in satisfactory shape, and there is frequent doubt as to whether the moisture contents are calculated on the dry or moist basis. It has therefore seemed desirable to assemble the most reliable of the available data, to determine experimentally the equilibria for many other common substances, and to present these data in a single article to which reference can readily be made.

It is obvious that in dealing with such materials, most of which are colloidal in nature and not of definite composition, there is no need to seek excessive refinement in the methods, but the values presented are believed to be correct at least within 0.5 per cent moisture for the particular sample tested, except for a few cases where special difficulties are mentioned.

TYPES OF HUMIDITY EQUILIBRIUM CURVES

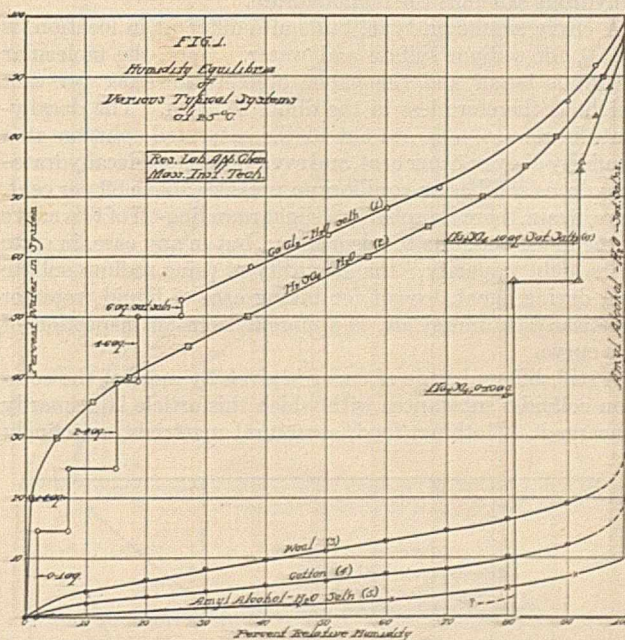
Before proceeding to a detailed consideration of specific substances, it may be well to consider briefly the various types of humidity equilibrium curves which are found for different systems. The vapor pressure data for various typical systems are shown in Fig. 1.

Throughout this article, equilibrium vapor pressures are plotted in per cent of that of pure water at the same temperature (25° C.) rather than in millimeters, because the former values change but little with temperature and they repre-

sent the "relative humidity" of the air with which they are in equilibrium.

Curve 2, for mixtures of sulfuric acid in water, is a typical vapor pressure curve for a system comprising water and some other liquid which is miscible therewith in all proportions. The very considerable affinity of the acid for the water is clearly shown by the height of the line, especially at very low humidities.

Liquids, such as amyl alcohol, which have much less affinity for water and are only partly miscible therewith, give a different type of curve, shown as No. 5 in Fig. 1. Here, even small amounts of water exert a very high vapor pressure,



only 2.2 per cent of dissolved water being in equilibrium with air of 50 per cent relative humidity. The vapor pressure increases somewhat less rapidly up to 9.8 per cent water, which is the limit of solubility of water in isoamyl alcohol. Any additional water then forms increasing amounts of a separate phase containing a small amount of dissolved isoamyl alcohol. The vapor pressure therefore remains constant (vertical line) over a wide range of water contents, until the alcohol phase entirely disappears.

Still a different type of curve is given by the system calcium chloride and water. Solutions of calcium chloride behave very much like those of sulfuric acid, except that the lowering of vapor pressure is somewhat greater, partly due to its lower molecular weight. Eventually a point is reached, however, when the water content drops to 53 per cent, where $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ separates out, giving two phases. From there on, the vapor pressure drops in a stepwise manner, as different pairs of hydrates come into existence. A single hydrate is stable, without changing compositions, over a certain range of vapor pressures, giving a horizontal line. When the next higher hydrate comes into existence the vapor pressure becomes constant while the relative amounts of the two phases change, giving a vertical line.

¹ Received May 8, 1922.

² Published as Contribution No. 52 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

³ Director, Research Laboratory of Applied Chemistry, M. I. T.

It will be noted that, in moderately or very humid air, calcium chloride will take up a greater proportion of its weight of water than sulfuric acid, and hence is, from that

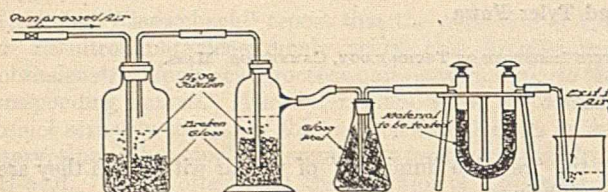


FIG. 2—APPARATUS FOR DETERMINATION OF HUMIDITY EQUILIBRIA

standpoint, a better drying agent; but that, for very low humidities, sulfuric acid is markedly superior to calcium chloride. The futility of attempting to get air even 99 per cent dry by the use of calcium chloride is indicated by these curves, although it should be said that they were determined on mixtures of two hydrates and that anhydrous calcium chloride probably adsorbs a very small amount of water at vapor pressures lower than the equilibrium pressure of the anhydrous salt plus the monohydrate.

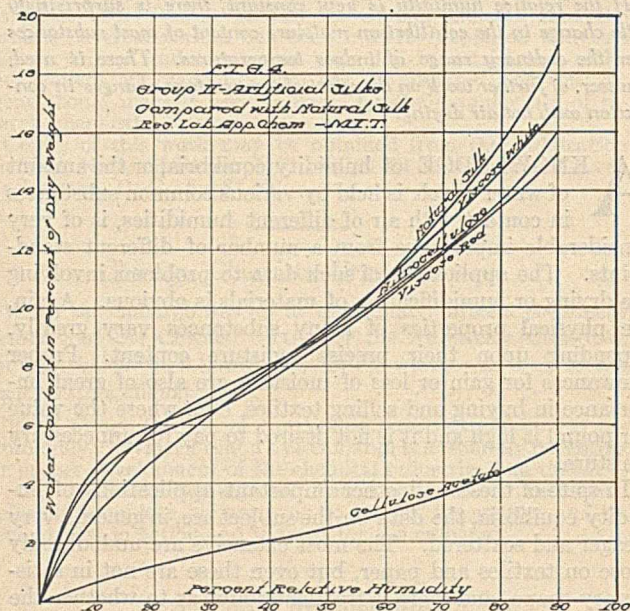
A curve similar in type, but quite different in location, is No. 6, for sodium sulfate and water. Here, the molecular weight is larger and the vapor pressure lowering per unit weight is therefore less in the dilute solution. The decahydrate begins to separate out of the saturated solution at a humidity of over 90 per cent, and even the system decahydrate-anhydrous salt has an equilibrium pressure above 80 per cent. Here, again, there is probably a slight rounding-off of this curve at the lower end, due to adsorption; but in any case, in spite of its high "capacity," the absurdity of using sodium sulfate as a drying agent, except for taking care of liquid water or practically saturated air, is apparent from an inspection of this curve.

A still different type of curve is given by most of the common colloidal substances with which this article is primarily concerned. Clothing, food, structural materials, and finely

divided solids tend to take up certain definite amounts of water corresponding to the humidity of the air. Typical curves are those for wool and cotton cloth (Nos. 3 and 4 in Fig. 1). Most textile materials and other organic colloids lie beyond these two limits, and finely divided solids in general still lower than this—in an entirely different range from drying agents such as calcium chloride and sulfuric acid. The vapor pressures of these colloidal materials are, of course, rather variable from sample to sample, as contrasted with the definite reproducible equilibria for hydrates and mixtures of pure liquids.

METHOD USED IN THE DETERMINATIONS

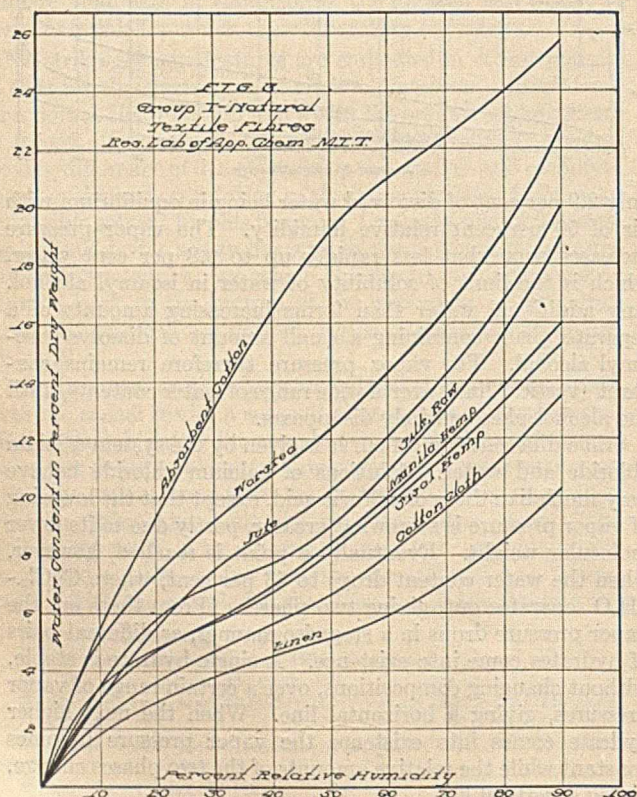
The method used in determining the equilibrium water contents of the substances considered in this article is described in detail in another paper by one of the authors,⁴ and therefore a brief description only will be given here.



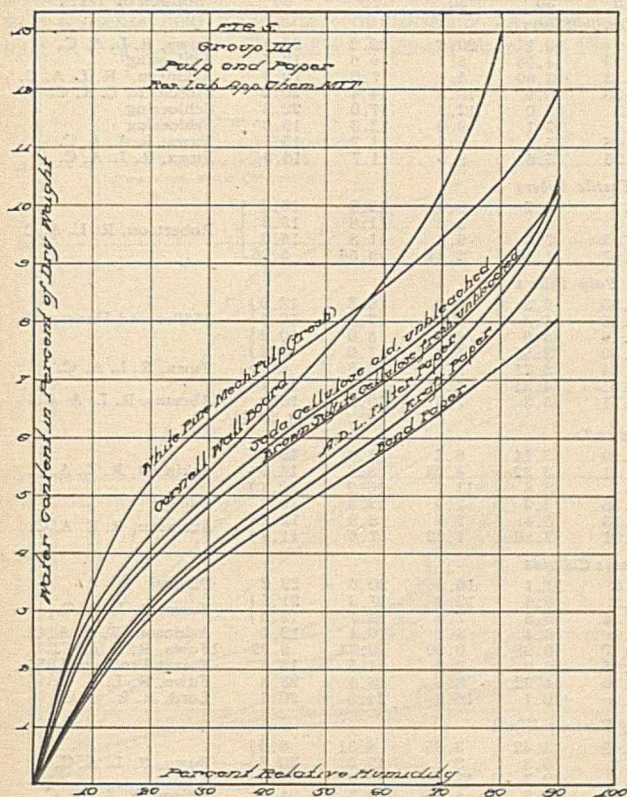
The substance is subdivided to present a reasonably large surface area, and placed in a weighed U-tube of about 50-cc. capacity. Air, which has been brought to the desired humidity by bubbling through the sulfuric acid bottles, is passed in a slow stream through the U-tube train, as shown by Fig. 2. Moisture equilibrium is generally reached in from 18 to 96 hrs., except in the case of some materials of a colloidal nature, such as soap and gelatin, which are more difficult of equilibration.

Each substance was brought to equilibrium successively in this manner at 15, 30, 50, 70, and 90 per cent relative humidity, after which saturated air was passed through the train for a short time and the same equilibrium points again determined by an approach from the saturated end, *i. e.*, at 90, 70, 50, 30, and 15 per cent relative humidity. Lastly, the dry weight of the sample was found by passing a stream of air, previously dried with phosphorus pentoxide, through the sample, the U-tube being immersed in a bath at about 50°C. This speeds up the approach of equilibrium at the dry end, which is otherwise quite slow, without giving appreciably different results from those obtained by much longer runs at 25°C. In general, these dry weights also check up well with the ordinary "oven-dry" weights at 105° or 110°C., though

⁴ Robert E. Wilson, "Humidity Control by Means of Sulfuric Acid Solutions with Critical Compilation of Vapor Pressure Data," *This Journal*, 13 (1921), 326.



a few organic colloids give up slightly more water under these conditions.



Most of the data presented have been determined in this laboratory, but data from the literature have also been included where they appear to be reasonably reliable. The source of the data for each substance and a brief description of the sample used are given in Table III.

While the data given are believed to be quite accurate for the individual sample tested, most of the materials are colloidal in nature, and the results will undoubtedly vary considerably for different samples of similar material. Indeed, a study of the humidity equilibrium curves is frequently valuable in throwing light on differences in the structure and properties of the same type of material.

The method of calculation of equilibrium moisture is best explained, perhaps, by the use of an actual illustrative example; that of cellulose acetate silk, for instance, is given in Table I.

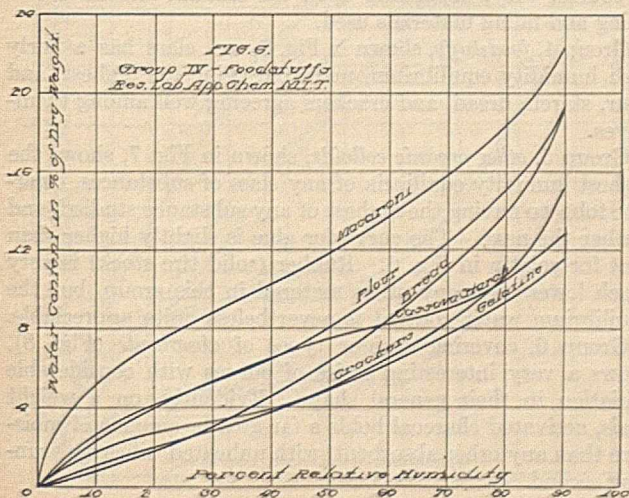
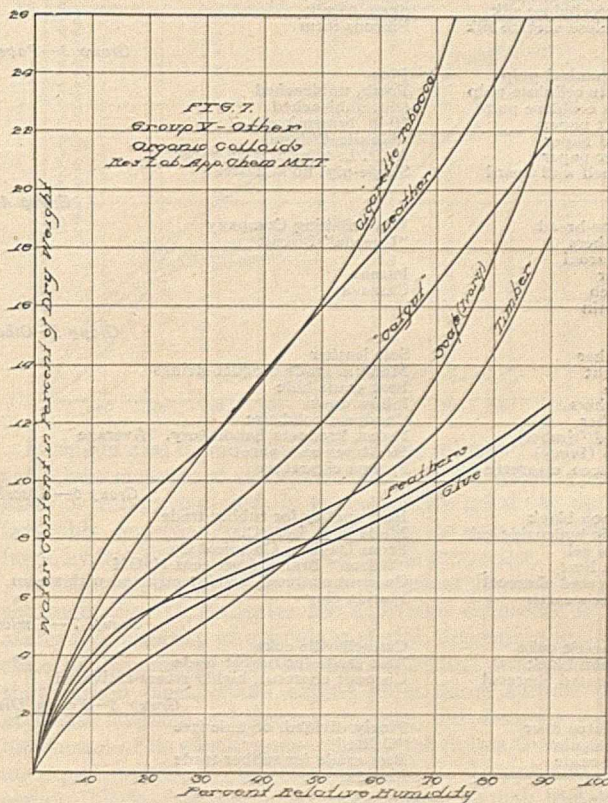


TABLE I—CALCULATION OF EQUILIBRIUM MOISTURE OF CELLULOSE ACETATE SILK

Relative Humidity Per cent	Equilibrium Wt. of Tube and Sample	Equilibrium Weight of Sample	Excess over Dry Weight	Per cent Water on "Dry Basis"	Average of "Up" and "Down" Runs
15	50.5280	6.4243	0.0620	0.97	0.97
30	50.5560	6.4523	0.0900	1.41	1.43
50	50.6200	6.5163	0.1540	2.42	2.44
70	50.6900	6.5863	0.2240	3.52	3.56
90	50.8000	6.6963	0.3340	5.25	5.25
70	50.6953	6.5916	0.2290	3.60	..
50	50.6224	6.5187	0.1561	2.46	..
30	50.5586	6.4549	0.0923	1.45	..
15	50.5275	6.4238	0.0612	0.96	..
0	50.4660	6.3623	0.0000	0.00	..



RESULTS

The equilibrium moisture for each substance was calculated according to the method of the illustrative example just given. The numerical data recorded in Table III are, however, in practically all cases the mean of the two equilibrium determinations; that is, the up run, and down run made on each sample. In Figs. 3 to 10, these data are presented in graphical form, arranged in several groups of related materials.

It will be noted that, while it is not possible to predict quantitatively the humidity equilibrium curve of a given substance (except in the case of a few pure compounds), a few generalizations can be made in this respect. These may be summarized according to Table II.

TABLE II

PER CENT WATER CONTENTS ON DRY BASIS		NATURE OF SUBSTANCES IN EACH CLASS
at 50 Per cent Relative Humidity	at 90 Per cent Relative Humidity	
0-4	0-6	Finely divided inorganic substances, carbon and lampblacks, coke, rubber, cellulose acetate silk
4-8	8-19	Foodstuffs (except macaroni), paper and pulp fibers, glue, fuller's earth, linen
8-12	13-26	Artificial and natural textile fibers (except cellulose acetate), macaroni, leathers, wood, soap, caoutchouc, ferric hydroxide gel
12-28	22-50	Absorbent cotton, leather, cigarette tobacco, silica gel, activated charcoal

TABLE III—EQUILIBRIUM MOISTURE CONTENTS

SUBSTANCE	DESCRIPTION OF MATERIAL	Per cent of Water on Dry Basis— Per cent Relative Humidity					SOURCE OF DATA
		15	30	50	70	90	
<i>Group 1—Natural Textile Fibers</i>							
Absorbent cotton	Sterile absorbent cotton "B & B"	8.9	10.1	20.6	22.2	25.8	Fuwa, R. L. A. C.
Cotton cloth	Sheeting	2.99	4.56	6.7	9.6	13.5	Schloesing ¹
Linen	Table-linen material	2.53	3.60	5.1	7.0	10.2	Atkinson, ² R. L. A. C.
Jute	Average several grades	4.33	6.9	10.2	14.4	20.2	Storch, R. L. A. C.
Wool	Worsted	6.3	9.0	12.2	17.0	22.9	Schloesing
Raw silk	Cheyennes	5.0	7.1	9.0	13.3	19.0	Schloesing
Sisal hemp	Strands from rope	4.48	5.6	8.3	11.7	15.1	Fuwa, R. L. A. C.
Manila hemp	Strands from rope	4.25	5.6	8.5	11.7	16.0	Fuwa, R. L. A. C.
<i>Group 2—Artificial Textile Fibers</i>							
White viscose silk	Skein of silk	5.6	6.7	9.4	12.9	16.8	Robertson, R. L. A. C.
Red viscose silk	Skein of silk	5.3	6.4	9.0	11.8	15.2	
Nitrocellulose silk	Skein of silk	3.95	7.0	9.1	11.8	16.0	
Cellulose acetate silk	Fibrous form	0.97	1.43	2.44	3.56	5.26	
<i>Group 3—Paper and Pulp Fibers</i>							
Mechanical pulp	Pine	4.55	6.3	7.9	9.5	12.0	Müller and Haussner ³
Sulfite cellulose pulp	Fresh, unbleached	3.35	5.8	6.3	7.8	10.5	
Soda cellulose pulp	Old, unbleached	3.49	5.0	6.6	8.0	10.2	
Kraft paper	60-lb. brown kraft	2.50	3.85	5.4	7.0	9.2	Fuwa, R. L. A. C.
Bond paper	"Manifest" bond	2.34	3.71	5.1	6.5	8.1	
Filter paper	A. D. L. quantitative paper	2.51	4.21	5.6	7.4	10.1	
Cornell wall board	Single-ply, no adhesive	3.71	5.3	7.5	10.3	13.0	
<i>Group 4—Foodstuffs</i>							
White bread	Ward Baking Company	0.99	3.14	6.2	11.0	19.0	Atkinson, R. L. A. C.
Crackers	"Uneceda" Biscuit	2.51	3.32	4.98	8.3	14.9	
Macaroni		6.5	8.8	11.7	16.2	22.1	
Flour	Patent	3.55	5.3	7.9	12.3	19.1	Bailey ⁴
Starch	Cassava	2.83	5.4	7.6	8.9	12.7	Atkinson, R. L. A. C.
Gelatin		1.01	2.80	4.92	7.6	11.4	
<i>Group 5—Other Organic Colloids</i>							
Leather	Sole leather	7.0	11.1	16.0	20.6	29.2	Phelps ⁵
Catgut	Medium grade racquet strings	6.2	8.6	12.0	17.3	21.7	Fuwa, R. L. A. C.
Glue	Best grade hide	4.24	5.8	7.6	10.7	12.5	
Feathers	Pillow down	5.0	6.4	8.1	10.4	12.7	Atkinson, R. L. A. C.
Rubber	Goodyear solid tire	0.17	0.28	0.60	0.74	0.99	Fuwa, R. L. A. C.
Wood (timber)	Forest Products Laboratory. Average	4.65	6.9	9.0	11.5	18.6	Forest Products Lab.
Soap (Ivory)	99.44 per cent pure!	3.36	4.62	8.4	18.4	23.8	Fuwa, R. L. A. C.
Tobacco, cigarette	Fatima cigarettes	8.9	10.1	16.0	24.5	50.1	Lord, R. L. A. C.
<i>Group 6—Absorbents of Various Kinds</i>							
Carbon black	Best quality for rubber trade	2.48	3.42	3.85	4.31	6.0	Fuwa, R. L. A. C.
Ferric hydroxide gel	Made in R. L. A. C.	5.2	6.8	8.1	12.6	20.0	
Silica gel	From Davison Chemical Co.	8.0	12.7	17.3	20.2	22.6	Wilson, R. L. A. C.
Soda lime	"Wilson" Brand, 5 per cent NaOH	2.0	3.5	6.5	11.6	24.0	
Activated charcoal	Coconut charcoal, highly activated with steam	9.5	22.8	28.3	30.0	32.7	Fuwa, R. L. A. C.
Fuller's earth	Florida clay	4.54	...	7.5	...	15.6	
<i>Group 7—Various Forms of Carbon</i>							
Domestic coke	Connellsville coke	0.33	0.60	1.02	1.48	1.89	Selvig and Kaplan ⁶
Carbon black	Best grade for rubber trade	2.48	3.42	3.85	4.31	6.0	Fuwa, R. L. A. C.
Activated charcoal	Coconut charcoal, highly steam-activated	9.5	22.8	28.3	30.0	32.7	
<i>Group 8—Finely Divided Inorganic Substances</i>							
Asbestos fiber	Finely divided, organic free	0.22	0.26	0.40	0.62	0.84	Fuwa, R. L. A. C.
Kieselguhr	"Celite"	0.50	0.88	1.40	2.00	3.19	
Zinc oxide	Best grade for rubber trade	0.17	0.29	0.36	0.41	0.59	
Kaolin	Florida	0.30	0.60	0.92	1.06	1.27	
Glass, wool		0.09	0.09	0.17	0.23	0.40	

¹ M. T. Schloesing, Jr., *Bull. soc. encour. ind. nat.*, 1893.² Mr. Atkinson's results were obtained at Northeastern University under the direction of the writers, and formed the basis of a Bachelor's thesis at that institution.³ Müller and Haussner, "Der Herstellung und Prüfung des Papiers," p. 1642.⁵ C. Phelps, M. I. T. Thesis, 1919.⁴ C. H. Bailey, *THIS JOURNAL*, 12 (1920), 1102.⁶ W. A. Selvig and B. B. Kaplan, *THIS JOURNAL*, 12 (1920), 783.

It is interesting to note that practically all of the curves have the same general shape, the water content rising comparatively rapidly at low and again at high humidities, and flattening out in the intermediate range between 20 and 60 per cent relative humidity.

Under Group 1, *natural textile fibers* (Fig. 3), it will be noted that wool, jute, and silk have the greatest affinity for moisture, while cotton and especially linen have the least. Absorbent cotton is, however, higher than any of the untreated fibers, presumably as a result of the effect of the severe treatment with alkali, etc., which changes the colloidal properties of the fibers.

The results on Group 2, *artificial textile fibers*, shown in Fig. 4, show a surprisingly close agreement between the equilibrium curves for the viscose and nitrocellulose silks and natural silk. Cellulose acetate, however, holds far less moisture than the others, which accords with its markedly different behavior on dyeing, etc. This should make it possible to use the acetate silk and also cellulose acetate films for certain purposes, where the other cellulose products would not be suitable.

Group 3, covering *pulp and paper fibers* of different types (Fig. 5), shows a very good concordance between the different

types of material. The two highest curves are for materials which contain large amounts of lignin (mechanical pulp and wall-board), while the fibers which are primarily pure cellulose check up very well. The kraft and bond papers will, of course, vary, depending upon the amount and nature of sizing and filling materials used.

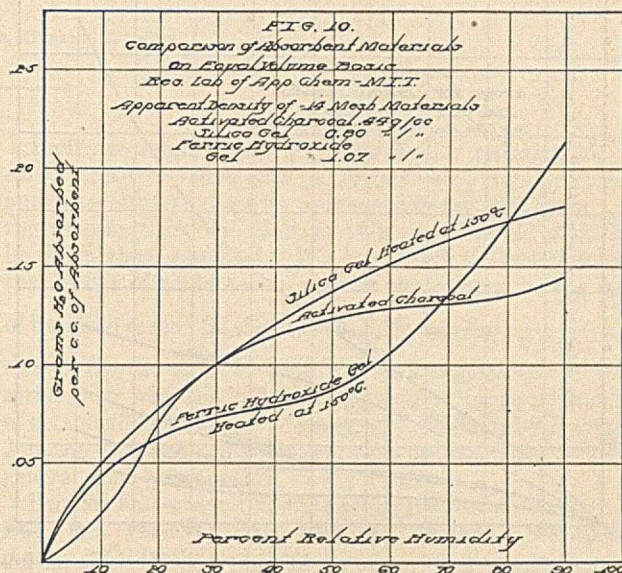
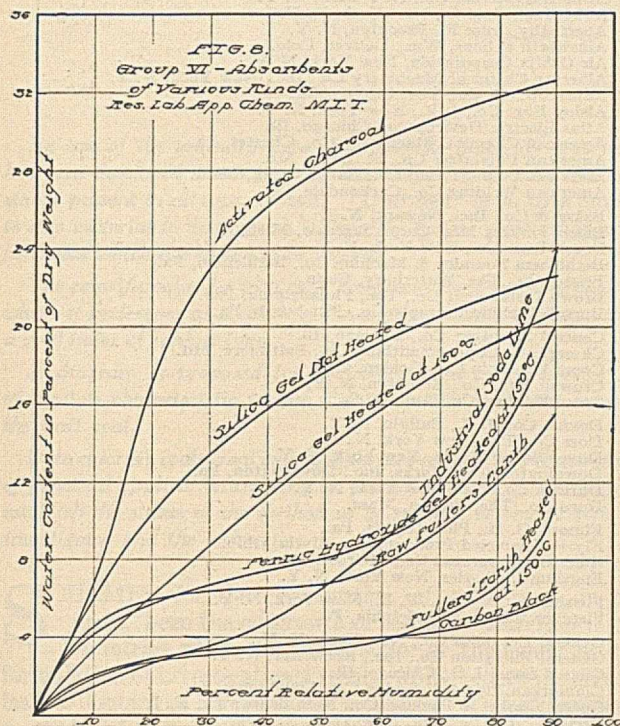
Group 4, *foodstuffs*, shown in Fig. 6, as a class has a fairly high humidity equilibrium, macaroni being the highest, and flour, starch, bread, and crackers agreeing well among themselves.

Group 5, *other organic colloids*, shown in Fig. 7, shows the highest humidity equilibria of any class of substances, cigarette tobacco having the highest of any substance studied, and leather the next. The curve for glue is slightly higher than that for gelatin in Fig. 6. Rubber (solid tire stock) is very much lower than any other material in this group, but the equilibrium water content is nevertheless quite appreciable.

Group 6, covering various types of *absorbents* (Fig. 8), shows a very interesting series of curves with considerable variation in their general shape. Evidently, on a weight basis, activated charcoal holds a far greater amount of moisture than any other absorbent, with unheated silica gel running second.

In the case of silica gel and fuller's earth, the same equilibrium was not readily attained when approached from opposite sides, there being quite a discrepancy between the moisture contents held even after equilibrating for periods as long as 3 or 4 days. This effect is shown clearly in Fig. 9,

because of its very low apparent density. By making the comparison on a volume basis, as in Fig. 10, it will be noted that there is a fairly close agreement between the curves for the three principal adsorbents, charcoal, silica gel, and ferric hydroxide gel, though their shape is markedly different.

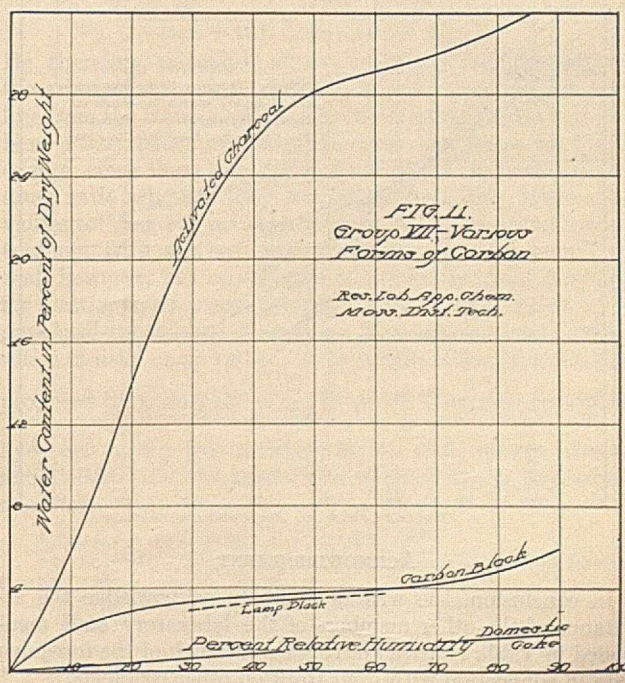
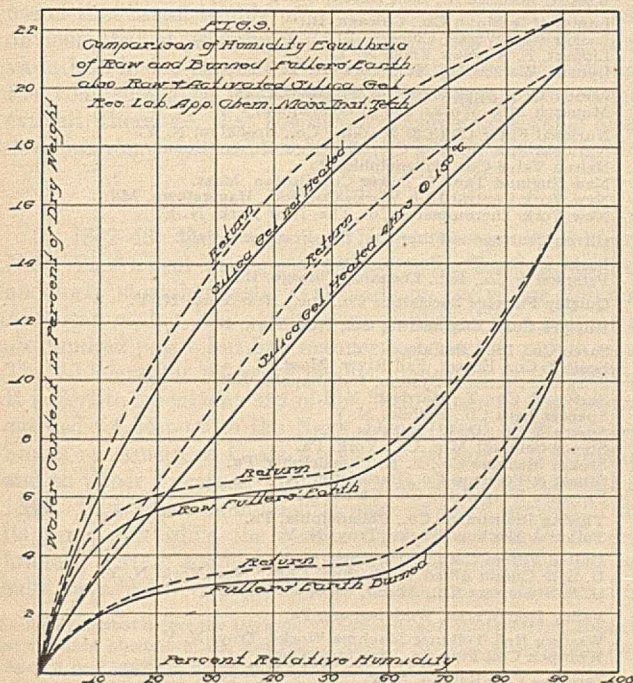


which shows the values obtained under the two sets of conditions. It also brings out clearly the effect of heating these types of absorbents even to 150°, which makes a marked and apparently permanent change in the amount of moisture which they hold at different humidities.

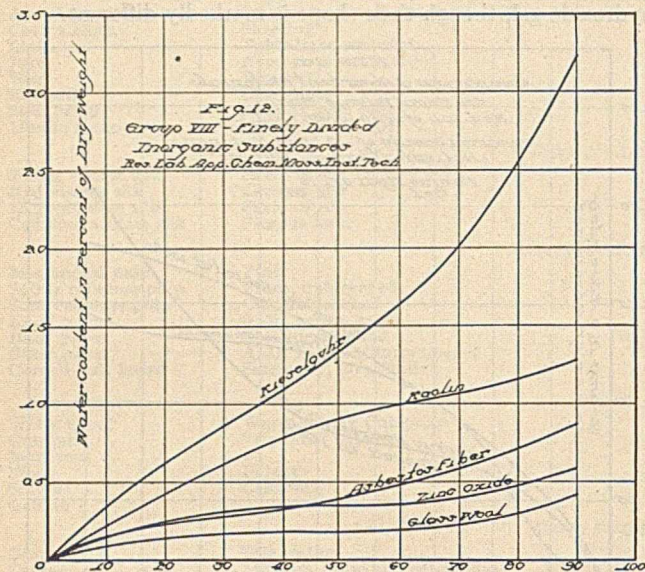
In comparing different absorbent materials, it is frequently the efficiency per unit volume rather than per unit weight which determines their comparative value for many uses. Charcoal, for example, shows up well on a weight basis

It should also be emphasized that the affinity for water is not a true measure of adsorptive efficiency for other types of gases or vapors and that, in general, silica gel shows up less favorably, and charcoal more favorably, on organic solvents, ferric hydroxide gel having intermediate properties.

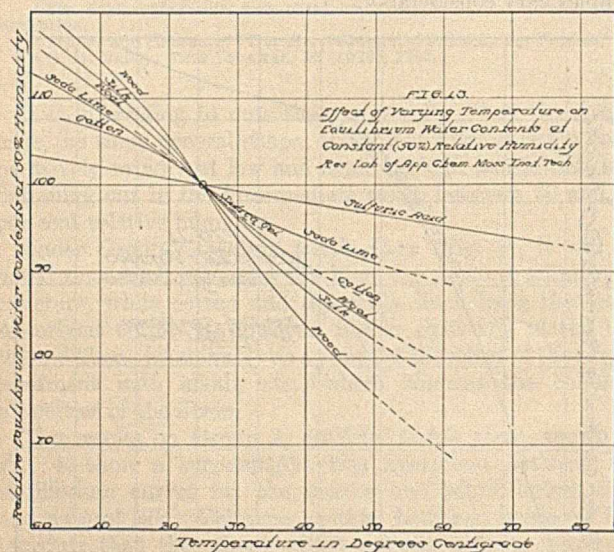
A study of the data for Group 7, various forms of carbon, shown in Fig. 11, indicates the enormous difference in the absorptive capacity of a single material, depending upon its state of dispersion. The average individual would assume that carbon black would expose much more surface than activated charcoal and this may be true; but, actually, either its amount or its effectiveness must be much less than that of an equal weight of activated charcoal. Lampblack and carbon black average about the same, though different samples vary considerably.



The finely divided inorganic solids, shown in Group 8, Fig. 12, have a characteristically low, but nevertheless definite, absorptive capacity for moisture, kieselguhr being the highest and kaolin the next, as might be expected.



The effect of temperature on humidity equilibria is an important question in many cases. It is common experience that heating up air, even for 20° or 30°, makes it a much more efficient drying agent, but this is due primarily to the decrease in its relative humidity rather than directly to the increase in temperature. If the relative humidity is kept constant, there is surprisingly little change in the equilibrium moisture content of most substances over the ordinary range of indoor or outdoor temperatures—an increase in temperature of 25° C. giving a moisture content around 85 per cent of that at the lower temperature. The effect of temperature changes on the equilibrium moisture content at 50 per cent relative humidity is shown in Fig. 13, for a few typical substances on which the data seem fairly reliable. This work should, however, be supplemented before the data are used to work out accurate schedules for hot air drying, etc.



ACKNOWLEDGMENT

In conclusion, the writers desire to acknowledge the assistance of the other members of the laboratory staff mentioned in Table III, who have secured much of the foregoing data in connection with their work on other problems.

Chemical Equipment Manufacturers Who Petitioned Congress

The petition to Congress to vote for the amendment extending the Dye and Chemical Control Act, which appeared on page 863 of our September issue, was signed by the following:

- Abbé Engineering Co., New York, N. Y.
- Abbé, Inc., Paul O., New York, N. Y.
- Abernethy, John F., Brooklyn, N. Y.
- Ainsworth & Sons, Wm., Denver, Colo.
- Air-O-Mix Corporation, New York, N. Y.
- Alberger Chemical Machinery Co., Inc., New York, N. Y.
- Albright-Nell Co., The, Chicago, Ill.
- Alsing Eng. Co., J. R., New York, N. Y.
- Atlas Electric Devices Co., Chicago, Ill.
- American Chemical Machinery Co., Chester, Pa.
- American Pulverizer Co., St. Louis, Mo.
- American Steam Pump Co., Battle Creek, Mich.
- American Welding Co., Carbondale, Pa.
- Baker & Co., Inc., Newark, N. J.
- Baker-Perkins Mfg. Corp., Saginaw, Mich.
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- Bristol Co., The, Waterbury, Conn.
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- Burrell Technical Supply Co., Pittsburgh, Pa.
- Central Scientific Co., Chicago, Ill.
- Chesapeake Copper Smithing Co., Baltimore, Md.
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- Dover Boiler Works, New York, N. Y.
- Downington Iron Works, Inc., Downington, Pa.
- Duriron Co., Inc., New York, N. Y.
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- Elmore, G. H., Philadelphia, Pa.
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- Fleisher & Co., Inc., W. L., New York, N. Y.
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- General Filtration Co., Inc., Rochester, N. Y.
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- Goetze Gasket & Packing Co., New Brunswick, N. J.
- Greiner Co., The Emil, New York, N. Y.
- Hardinge Co., Inc., New York, N. Y.
- Harrisburg Pipe & Pipe Bending Co., Harrisburg, Pa.
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- Hoskins Manufacturing Co., San Francisco, Calif.
- Hubbard's Sons, Norman, Brooklyn, N. Y.
- Hydro & Chemical Tank Co., New York, N. Y.
- Independent Filter Press Co., Inc., Brooklyn, N. Y.
- Industrial Filtration Corp., New York, N. Y.
- Johnson Co., John, Brooklyn, N. Y.
- K-B Pulverizer Co., Inc., New York, N. Y.
- Keasbey & Mattison Co., New York, N. Y.
- Kelly & Jones Co., The, New York, N. Y.
- Kent Machine Works, Brooklyn, N. Y.
- Kestner Evaporator Co., Philadelphia, Pa.
- Kimble Glass Co., Vineland, N. J.
- Knight, Maurice A., East Akron, Ohio.
- Lammert & Mann Co., Chicago, Ill.
- Lasker Iron Works, Chicago, Ill.
- Lippert, F. A., New York, N. Y.
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- Mine Safety Appliances Co., Pittsburgh, Pa.
- Monarch Mfg. Works, Inc., Philadelphia, Pa.
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- Nelson Valve Co., Philadelphia, Pa.
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- New York Central Iron Works Co., Inc., Hagerstown, Md.
- New York Thermometer Co., The, New York, N. Y.
- Oliver Continuous Filter Co., San Francisco, Calif.
- Parks-Cramer Co., Boston, Mass.
- Peterson & Co., Inc., Leonard, Chicago, Ill.
- Quigley Furnace Specialties Co., Inc., New York, N. Y.
- Ruggles-Coles Engineering Co., New York, N. Y.
- Sarco Co., Inc., Buffalo, N. Y.
- Scott & Co., Ernest, Fall River, Mass.
- Schwartz Sectional System, Indianapolis, Ind.
- Shriver & Co., T., Harrison, N. J.
- Spencer Lens Co., Buffalo, N. Y.
- Sperry & Co., D. R., Batavia, Ill.
- Stacey-Schmidt Mfg. Co., York, Pa.
- Stokes Machine Co., F. J., Philadelphia, Pa.
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- Swenson Evaporator Co., Chicago, Ill.
- Thwing Instrument Co., Philadelphia, Pa.
- Tolhurst Machine Works, Troy, N. Y.
- United Filters Corp., New York, N. Y.
- U. S. & Cuban Allied Works Eng. Corp., New York, N. Y.
- U. S. Stoneware Co., Akron, Ohio.
- Valley Iron Works, Williamsport, Pa.
- Western Ref. Tolhurst Machine Works, Troy, N. Y.
- Whitlock Coil Pipe Co., Hartford, Conn.
- Zaremba Co., Buffalo, N. Y.

The Classification of Coal¹

By S. W. Parr

UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

By use of the ordinary data of proximate analysis, a formula has been developed which gives the true value for the pure coal substance present in all types of coal. "Unit coal" is the term applied to this material to distinguish it from the factors obtained by other formulas which are shown to be in error.

The calorific value for unit coal, because of the direct modification which it undergoes as a result of the oxygen content, is shown to be a good index of rank or type.

A diagram is proposed for indicating rank which makes use of the two characteristic factors, volatile matter and heat value of the unit coal.

Data covering coals from widely separated regions and illustrations of practical application covering an extended period of time seem to establish the status of the method as of possible service to both the investigator and the technician.

SCHMES for the classification of coal have, in the main, been the outgrowth of technical activities in the countries where they originate, or they may be the formulation of investigational results which reflect the geological or botanical or chemical activities of their authors. A study of the development of methods of classification as an evolutionary process is exceedingly interesting and valuable, but would exceed the limit allowable for a paper of this sort. An accumulation of information, however, is now available which suggests the possibility of formulating a scheme which may serve the needs of both the investigator and technician to an extent which will justify its adoption as a general working proposition. This is a rather ambitious project, it must be admitted, but the end is worth the effort.

Without any question, the most characteristic constituent of a coal is the volatile matter. But if we attempt to make use of that factor simply on a percentage basis, it is at once obvious that it is subject to irregularities resulting from variations in the amount of extraneous matter, even though the coal substance itself remains the same. It becomes evident, therefore, that the use of a percentage value alone develops many inconsistencies.

HISTORICAL

In 1842-43, there was established at the Washington Navy Yard a coal testing plant where more than one hundred and forty steaming tests were made on forty-four different American coals. The results were published in a volume of six hundred pages, but in a manner to be lost to public view. The bibliographic reference in this connection is interesting. It is Senate Document 386 of the 28th Congress, 1st Session, entitled "A Report to the Navy Department of the United States on American Coals Applicable to Steam Navigation and to Other Purposes," by Walter R. Johnson,² printed in 1844. This was a monumental piece of work, especially for its time, and while the results have now mainly historic interest, certain methods employed in summarizing the results have had a very pronounced influence on classification.

¹ Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² Walter R. Johnson, Professor of Physics and Chemistry at the University of Pennsylvania, 1839-43.

Professor Johnson had a propensity for reducing his results to relative values with reference to each significant item and tabulating the factors progressively for each item. At the present time, the plotting of a curve would doubtless be the method employed. It is interesting to note, however, that in one of his tables he devotes one column to the ratio

of the fixed carbon to the volatile hydrocarbons, $\frac{C}{V. h-c.}$, and

these ratios are seen to have a certain agreement in their serial order with the "relative evaporation by equal weights of combustible matter." No suggestion is made by Professor Johnson as to the possible use such ratios might serve in general coal classification.

Persifer Frazer, according to a paper read before the Wilkes-Barre (1877) meeting of the American Institute of Mining Engineers,³ evidently had been seeking for some method of improving upon the scheme of classification proposed by his predecessor, Professor Rogers,⁴ who made use of percentage values taken from Johnson's report and elsewhere and referred to the total coal as received. In seeking to eliminate the inconsistencies resulting from wide variation in the ash and moisture, Frazer brought into use the ratio idea of Johnson, arguing that if the fixed carbon and volatile matter were calculated to the ash- and moisture-free basis, the extraneous matter would be excluded. Then, by putting the two values into a ratio, a series of ranking index numbers would result which he proposed to group in a manner to indicate a system of classification. The odd thing about Frazer's discussion is the fact that he seems to think it essential to calculate all values to the pure coal condition so that his two factors for C (fixed carbon) and V. h-c. (volatile hydrocarbons) will equal 100 per cent. Thus,

$$\frac{C}{1-(\text{ash} + W)} + \frac{V. h-c.}{1-(\text{ash} + W)} = 100$$

He, therefore, calculated all the analytical data available to the ash- and water-free condition in order to obtain his ratios free from the influence of extraneous or adventitious material. Now a very little inspection will show that this is all wasted energy, since these two values for C and V. h-c. will give the same ratio whether they are taken from the "pure coal" values totaling 100 per cent or from the "as received" values totaling, with the ash and moisture, 100 per cent. His zeal, however, has caused him to err in the right direction; for a ratio, to have any significance, must relate solely to the pure coal substance. Variations from this principle furnish ratios of little or no value. Note in this connection the ratio proposed by Campbell⁵ of $\frac{C}{H}$ in which H includes all of the hydrogen of the free moisture in the coal, though Strahan and Pollard⁶ use the same ratio referred to the dry ashless material.⁷

³ *Trans. Am. Inst. Mining Eng.*, 6 (1877), 430.

⁴ H. D. Rogers, "The Geology of Pennsylvania, a Government Report," 2 (1858), 991.

⁵ *U. S. Geol. Surv., Professional Paper* 48, Part I, 156.

⁶ "Coals of South Wales," 1915.

⁷ Numerous errors are evident in Frazer's paper; as, for example, his statement that in the data available at that time, the factor for water was included in the volatile matter. All Johnson's data give the moisture values as distinct from the volatile matter.

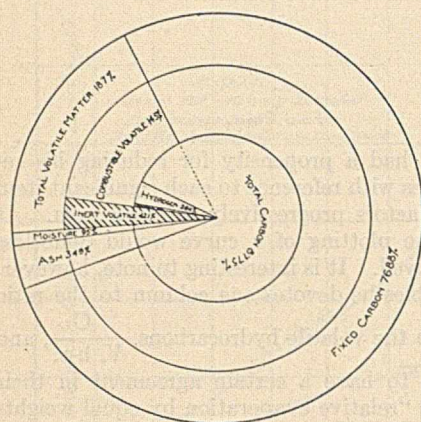
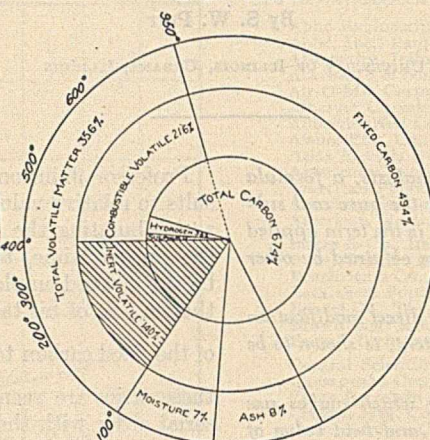
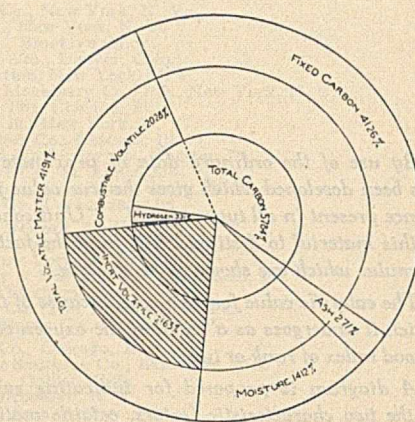
ANALYSIS OF EASTERN
COALSANALYSIS OF A SEMI-BITUMINOUS COAL
(POCAHONTAS) SHOWING CONSTITUENTS
IN RELATIVE PROPORTIONSANALYSIS OF ILLINOIS
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SHOWING CONSTITUENTS IN
RELATIVE PROPORTIONSANALYSIS OF LIGNITIC
COALSANALYSIS OF A LIGNITIC OR BROWN
COAL SHOWING CONSTITUENTS
IN RELATIVE PROPORTIONS

FIG. 1

In a former system of classification proposed by the author,⁸ the ratio employed was $\frac{VC}{C} \times 100$, in which C represented

the total carbon and VC that part of the carbon which associates itself with hydrogen to form the volatile hydrocarbons. This ratio is free from inorganic variables and has the advantage with respect to the greater accuracy of obtaining one of the factors, the total carbon. It was recognized in that discussion that another significant element entered into the case which could not be covered conveniently by any ratio. This was the inert part of the volatile matter or oxygen compounds of the coal. In that article, no satisfactory scheme was proposed for taking account of that constituent which we now recognize not only as a part of the true coal substance, but as a very significant factor which, to an equal extent with the volatile matter, determines the rank of a coal.

PROPOSED BASIS OF CLASSIFICATION

As illustrative of a method for taking account of the inert volatile matter, attention is called to the cross-hatched areas in each of the three diagrams in Fig. 1. These areas represent the oxygen compounds of the actual coal substance in each type: (1) a low volatile eastern coal, (2) a high volatile Illinois coal, and (3) a lignitic coal. It is now suggested that the most direct method of classification, and one which would give expression to this constituent, would be the calorific value of the pure coal substance. It should be recognized at the outset, however, that the factors for ash and moisture must not only be very accurately determined, but one disturbing factor, the sulfur, should be eliminated altogether. While a small amount of sulfur is always present in organic form and is a true part of the coal material, the main part, as a rule, is in the form of FeS_2 . It is evidently of secondary formation and is so irregular in amount as to indicate the desirability of eliminating it entirely from the actual coal substance. A glance at Fig. 2, showing the organic and pyritic sulfur in different locations in the same mine, is sufficient evidence without further comment as to

⁸ S. W. Parr, "The Classification of Coals," *J. Am. Chem. Soc.*, **28** (1906), 1425.

the desirability of counting the sulfur as part of the extraneous matter.⁹

One other ingredient should be taken account of. In the case of Eastern coals where the ash is low, it has only minor significance, but in lower grade coals, where the ash will average 16 to 18 per cent and may sometimes reach 25 or 30 per cent, it is important. This is the volatile material, chiefly water of hydration, which is discharged at a red heat from the shaley constituents of the ash. With this material assigned to its proper place, along with the sulfur as part of the ash, we are in a position to appreciate the significance of the heat value for the pure coal substance as unaffected by mineral impurities of any sort.

CORRECTION OF FACTORS

This brings us to the method of correcting the factors as determined in the ordinary process of proximate analysis. Fortunately, it resolves itself into a very simple formula. It should be noted that the first description of this formula with a detailed account of its derivation was published in 1909.¹⁰

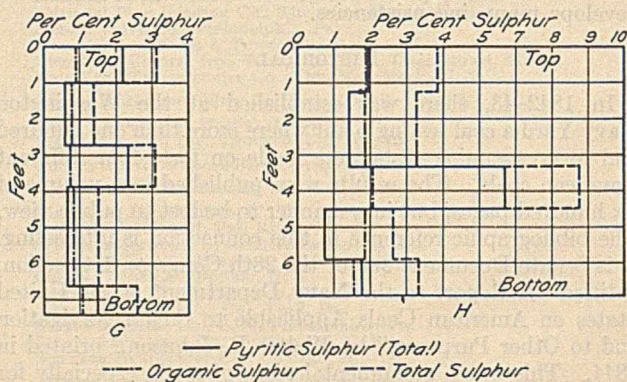


FIG. 2

⁹ Yancey and Fraser, "The Distribution of the Forms of Sulfur in the Coal Bed," *Univ. of Illinois Engineering Expt. Sta., Bulletin 125* (cooperative with U. S. Bureau of Mines and Illinois State Geological Survey); *THIS JOURNAL*, **13** (1921), 35.

¹⁰ Parr and Wheeler, "Unit Coal and the Composition of Coal Ash," *Univ. of Illinois Engineering Expt. Sta., Bulletin 37*; *THIS JOURNAL*, **1** (1909), 636.

The application at that time was solely in connection with the calculation of calorific values and had no reference to its use as a classification medium. After long-continued use with all types of coal, the marked accuracy of the formula as first proposed has led inevitably to its use as a classification factor.

It is not necessary to repeat here in detail the derivation of the formula. Its fundamental principles may be readily shown as follows:

Assuming the coal values as derived from analysis to be on the dry basis, then:

$$\text{Non-coal} = \text{Ash as weighed} + \frac{5}{8} S + 0.08 (\text{ash} - \frac{10}{8} S) \quad (1)$$

Combining and simplifying, we have Equation 2.

$$\text{Non-coal} = 1.08 \text{ ash} + \frac{21}{40} S \quad (2)$$

Hence, to derive the heat value for the unit coal, Equation 3 results.

$$\text{Heat value in B. t. u. for unit coal} = \frac{\text{Indicated B. t. u.} - 5,000 S}{1.00 - (1.08 \text{ ash} + \frac{22}{40} S)} \quad (3)$$

In Equation 1, it may be explained that the addition of $\frac{5}{8} S$ corrects the ash, as weighed, back to the form in which the sulfur was weighed in the original sample, namely FeS_2 . The factor in Equation 2 which increases the ash as weighed by 8 per cent is really an arbitrary constant, though it was derived experimentally in the first place by taking the average loss (not including organic matter) on ignition of a number of shales from the Illinois coal measures. It is doubtless mainly water, but may have some carbon dioxide from carbonates, or even sodium chloride, but obviously it should not be applied to the iron pyrites which is shown to be subtracted as Fe_2O_3 from the ash as weighed, the 8 per cent being applied to the remainder only. Equation 3 is derived from Equation 2, by subtracting in the numerator the heat due to the burning of the sulfur and the formation of Fe_2O_3 and in the denominator changing slightly the fraction $\frac{21}{40}$ to $\frac{22}{40}$, as being in the direction of simplifying the calculation as well as promoting accuracy by compensating slightly for the sulfur not in the pyritic form.

TESTS OF FORMULA

Now while a certain basis in theory may thus be set forth in defense of the formula, it would still be of little value unless it could be proved out in actual use as correct. Several methods suggest themselves. Obviously a coal with high ash from the same mine, or from the same sample by use of the "sink" and "float" method of separation, would respond unfavorably if the 8 per cent constant as applied to the ash were wrong. If this factor is correct, then so far as ash variations are concerned, the B. t. u. values for unit coal should calculate out to substantially the same number. Similarly, the sulfur corrections, when applied to wide variations in sulfur in the same sample or in samples from the same mine, should not produce a divergence in the thermal values when calculated to the unit basis. A great mass of data has accumulated from which only a limited number of illustrations can be given. However, they are typical and cover widely separated localities and practically all types of coal.

Table I is an assembly of results from samples which have been subjected to the "sink" and "float" process. By this procedure, each sample is divided into two parts with widely different values for the ash and sulfur. Manifestly the calculation of the indicated heat value to the corresponding value for the unit coal substance furnishes a crucial test for the suitability of the factors chosen for correcting the ash with reference to water of hydration and for sulfur.

If space permitted, very interesting evidence of an indirect character could be submitted in substantiation of the formula adopted. At least two other methods have been used to a greater or less extent for deriving the pure coal substance. If we compare the results obtained by use of these formulas

with the one here proposed, the discrepancies resulting in the case of sink and float samples of the same coal afford positive confirmation of the value of the new formula. A tabulated selection of a few cases only can be given in this connection.

TABLE I—COMPARATIVE VALUES OF PURE OR "UNIT" COAL

		Water	Ash	Sulfur	B. t. u.		
					Actual	Unit Coal	Dif.
1—Grundy County, Ill.	Sink	0.00	21.99	5.00	10,735	14,262	
	Float	0.00	4.57	1.44	13,475	14,217	+45
2—Williamson County, Ill.	Sink	0.00	18.28	1.37	11,731	14,667	
	Float	0.00	4.34	1.07	13,970	14,690	-23
3—Vigo County, Ind.	Untrtd.	0.00	16.84	7.62	11,790	14,698	
	Float	0.00	4.27	3.08	13,870	14,638	+60
4—South Africa	Sink	1.66	18.94	2.28	11,680	15,093	
	Float	1.63	6.06	1.38	13,703	15,065	+28
5—South Africa	Sink	1.82	15.24	1.80	11,847	14,799	
	Float	2.07	8.88	0.87	12,989	14,779	+20
6—South America (Brazil)	Sink	3.59	49.25	2.58	5,922	14,162	
	Float	5.97	17.24	0.68	10,602	14,127	+35
7—Walker County, Ala. (Pratt seam)	Sink	1.00	16.14	0.83	12,467	15,370	
	Float	1.20	4.40	0.85	14,384	15,371	-1
8—Jefferson County, Ala. (Mary-Lee seam)	Sink	0.92	23.70	1.23	11,246	15,620	
	Float	1.04	9.78	0.99	13,683	15,576	+44
9—Bituminous from W. Va.	Sink	1.15	4.96	0.76	14,373	15,443	
	Float	1.20	3.40	0.60	14,616	15,416	+27
10—Cannel from Kentucky	Sink	1.20	39.04	2.87	8,908	16,179	
	Float	0.97	13.40	1.74	13,560	16,205	-26
11—Anthracite from Pa.	Sink	0.70	16.75	1.07	12,280	15,232	
	Float	0.86	7.20	0.72	13,795	15,166	+66

TABLE II—COMPARISON OF HEAT VALUES FOR "PURE COAL SUBSTANCE" AS CALCULATED BY THREE METHODS FROM ANALYTICAL DATA ON "DRY COAL"

	Ash	Sulfur	B. t. u.	Calculated B. t. u.		
				a	b	c
Williamson Co., Ill.						
Sink	17.75	1.15	11,766	14,306	14,451	14,608
Float	4.08	0.99	13,924	14,535	14,644	14,623
DIFFERENCE.....				229	193	15
Franklin Co., Ill.						
Sink	18.00	0.57	11,639	14,194	14,236	14,474
Float	4.64	0.54	13,765	14,436	14,492	14,512
DIFFERENCE.....				241	256	38
Perry Co., Ill.						
Sink	22.17	1.15	10,922	14,033	14,183	14,413
Float	4.22	0.86	13,763	14,369	14,464	14,452
DIFFERENCE.....				336	281	39
$a = \frac{\text{B. t. u.}}{1.00 - A}; \quad b = \frac{\text{B. t. u.} - 4050 S}{1.00 - (A - S)}; \quad c = \frac{\text{B. t. u.} - 5000 S}{1.00 - (1.08A - \frac{22}{40} S)}$						

The derivation of a , b , and c may be understood from the following:

The expression B. t. u. is the indicated heat value, as obtained directly by means of the calorimeter. A is the ash as weighed, and S is the sulfur in per cent.

The method under a is the usual one employed by the engineer for determining the heat values for "combustible."

Under b , the method employed by Lord and Haas for determining the value of H , *i. e.*, the heat to be credited to the pure coal substance free from moisture, ash, and sulfur.¹¹

Under c , the formula is that for "unit coal" and has already been discussed.

Note that the analytical values are on the "dry coal" or moisture-free basis. Hence W for water is not introduced into the formulas.

For the reason that a zone of heat values may be indicated or prescribed for groups or types, a method of classification is therefore suggested as a result of the preceding discussion as to the true heat value of the unit coal substance, as shown in Table III.

TABLE III—CLASSIFICATION OF FUEL TYPES BY HEAT VALUES FOR UNIT OR ACTUAL ORGANIC SUBSTANCE

Cellulose and wood.....	6,500 to 7,800
Peat.....	7,800 to 11,500
Lignite, brown.....	11,500 to 13,000
Lignite, black, or sub-bituminous coal.....	13,000 to 14,000
Bituminous coal (mid-continent field).....	14,000 to 15,000
Bituminous coal (eastern field).....	15,000 to 16,000
Semianthracite and semibituminous.....	15,500 to 16,000
Anthracite.....	15,000 to 15,500

¹¹ *Trans. Am. Inst. Mining Eng.*, 27 (1898), 259; also Lord and Somermeier, "Report on Coal," 4th Geol. Surv., Ohio, 1908, 268.

The groups designated in Table III have been given the names as first proposed by Professor Rogers. These had become sufficiently established at the time of Frazer's paper to make it seem advisable for him to continue their use.¹² Campbell,¹³ at a still later date, follows the same general nomenclature and it does not seem wise now to introduce changes in these general and well-established names.

One fundamental criticism has always arisen concerning the use of heat values for designating coal rank. This relates to the lower values for anthracites which bring them into the same class with certain coals of the bituminous type.

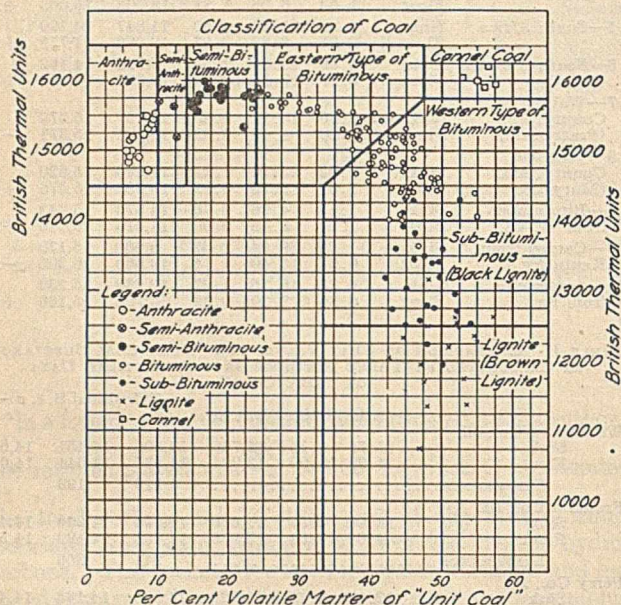


FIG. 3

This feature is really a virtue from the standpoint of the unit coal values as we have been discussing them. How therefore to incorporate this property in a classification scheme has been a problem. It has been solved in a very satisfactory manner by use of a two-dimension diagram, as shown in Fig. 3.¹⁴

In this chart, the percentage values for unit volatile matter have been located on the horizontal axis and the unit heat values on the vertical. By this means, the low volatile coals of the anthracitic type are segregated from the high volatile coals of the Illinois type even though their heat factors are closely related.

The values in the diagram have been calculated mainly from analytical data published by the U. S. Bureau of Mines.¹⁵ In this way coal samples from widely separated regions are represented.

The dividing lines have been chosen arbitrarily and at even hundreds, but it is interesting to note that for most of the zones there is a marked thinning out of the group representatives at the lines of division. As would be expected, there is more of a blending between the lignites and their neighbors, but in those instances where a sample seems to be out of place it is an even chance that the collector who named the sample was wrong in his diagnosis. At least, the author would hold that the unit B. t. u. is a safer criterion for

designating the rank than the physical characteristics which governed the designation at the locality where the samples were taken.

The cannel arrange themselves in a distinct group which reveals at a glance their true characteristics. Similarly, the eastern bituminous of the high volatile type are sharply segregated from the western bituminous as a result of their difference in oxygen or inert volatile content. The names "eastern" and "western" bituminous, however, are not well chosen and should be replaced by names or letters which would be universally applicable.

A word of explanation may be necessary concerning the method of deriving the percentage factor for the unit volatile matter. If we accept the factors as adopted for correcting the ash as weighed, it is seen that the chief constituents entering into those corrections are 8 per cent for the water of hydration of the clayey matter and the addition of $\frac{5}{8}$ S to restore the ash to the condition as weighed out in the sample. Now these values are in fact the errors that should be assigned to the volatile matter in the ordinary process of determination, where the 8 per cent of water is driven off at a red heat and approximately $\frac{1}{2}$ the sulfur is discharged from FeS_2 . The fixed carbon, therefore, has not been appreciably affected, since the errors of the volatile matter naturally appear in the ash as weighed, thus leaving the carbon by difference in substantially its true relationship to the original coal. Hence, to derive the fixed-carbon value on the unit coal basis, we would simply apply the standard formula for deriving the unit coal, thus:

$$\text{Unit fixed carbon} = \frac{\text{Fixed carbon as determined}}{1.00 - (1.08 A + \frac{22}{40} S)}$$

and from this, by difference:

$$\text{Unit volatile} = 1.00 - \text{unit fixed carbon}$$

TABLE IV

(Calculated to "as received" basis having normal variations of moisture, ash, and sulfur, as indicated. Unit coal: 14,300)

GENERAL LOCATION BY COUNTIES	Coal Bed	Ash	Sulfur	B. t. u. Calculated to Coal "as Received" with 12 Per cent Moisture	B. t. u. Calculated to Coal "as Received" with 14 Per cent Moisture
Sangamon south of Auburn	6	10	4	10,925	10,639
		11	4	10,771	10,484
Perry	6	12	4	10,616	10,330
		13	4	10,462	10,176
Randolph	6	14	4	10,308	10,021
		15	4	10,154	9,867
Clinton	6	16	4	10,000	9,712
		17	4	9,846	9,558
Madison	6	18	4	9,692	9,403
		19	4	9,538	9,250
Montgomery	6	20	4	9,384	9,094

TABLE V—COAL INDEX NUMBERS

	Moisture	Ash	Sulfur	A Unit Coal	B Index No.	
1—Anthracite, Scranton, Pa.	Sink	0.70	16.75	1.07	80.62	124.03
	Float	0.86	7.20	0.72	90.96	109.94
2—Bituminous, W. Va.	Sink	1.15	4.96	0.76	93.07	107.45
	Float	1.20	3.40	0.60	94.80	105.48
3—Walker Co., Ala. (Pratt seam)	Sink	1.00	16.14	0.83	81.11	123.29
	Float	1.20	4.40	0.85	93.58	106.86
4—South Africa	Sink	1.82	15.24	1.88	80.73	123.87
	Float	2.07	8.80	0.87	87.86	113.83
5—Brazil, So. America	Sink	3.59	49.25	2.58	41.81	239.17
	Float	5.97	17.24	0.68	75.08	133.26
6—Williamson Co., Ill.	Sink	0.00	18.28	1.37	79.51	125.77
	Float	0.00	4.34	1.07	94.27	105.57
7—Grundy Co., Ill.	Sink	17.28	5.27	2.33	75.48	132.49
	Float	0.00	6.37	2.82	91.57	109.20
8—Vermillion Co., Ill.	Sink	14.45	9.34	2.55	74.06	135.02
	Float	0.00	10.92	2.98	86.57	115.51
9—Franklin Co., Ill.	Sink	9.04	8.56	1.45	80.92	123.57
	Float	0.00	9.41	1.59	88.97	112.39
10—Alberta, Canada C. P. R. Synd.	Sink	1.39	27.50	0.85	68.45	146.09
	Float	1.17	3.02	0.72	95.18	105.06

¹² See Frazer's communication in defense of his classification, *Am. Inst. Mining Eng., Bimonthly Bulletin*, January 1906, 241.

¹³ U. S. Geol. Surv., *Professional Paper* 100-A.

¹⁴ From an unpublished thesis for the Master's degree, by E. B. Vliet, University of Illinois, 1918.

¹⁵ Values obtained from analysis of coals found in *Bur. Mines, Bulls.* 16, 22, 85, 123, and U. S. Geol. Surv., *Bull.* 621.

By this means, it will be seen that we have a very definite means of separating the 100 per cent unit coal into its two constituents, fixed carbon and volatile matter, thus fulfilling the preliminary argument that a ratio to be of value must exclude all extraneous matter. These two unit values may be expressed either as a ratio or a percentage, since together they equal 100 per cent, but the percentage values are employed for plotting in diagrammatic form, so as to indicate the comparison to better advantage.

Numerous additional illustrations of the practical value of the unit coal formula and the factors that accompany it might be given. For example, in Table IV, a certain area in Illinois is shown wherein the unit heat value for the coal produced averages 14,300 B. t. u. Assuming certain values for moisture, ash, and sulfur in the coal as marketed, a heat value for a number of average commercial conditions for the coal as delivered has been derived by reversing the calculation, starting from the accepted unit coal value. If the output from any specific mine in that region is known to have a unit coal value of 14,300 B. t. u., the calculated values for the various assumed amounts of impurities will be accurate to

within 0.5 per cent of the calorimetric indications, entirely comparable to duplicate results by the same operator on the same sample. Many methods for utilizing such a table or other values deducible by the same formula will readily suggest themselves—such as checking guaranties on coal bids, verifying the samples submitted as to their agreement with the gross shipment, detecting errors in calorimetric results, calculating calorific values in the absence of an instrument, obtaining the variable in heat value for each unit of ash, being exactly 154 units in this particular tabulation, etc.

One other table is submitted as having possible value in matters of every-day concern. In Table V, Column A, are listed the values for the unit coal in per cent of the coal as received. These values are derived simply by application of the unit coal formula incorporating, of course, "W" for the moisture present. Column B gives simply the reciprocal of the values under A and represents the number of pounds of each sample which would be required to furnish 100 lbs. of actual combustible or pure coal substance.

The Electric Steam Generator¹

By Horace Drever

ELECTRIC FURNACE CONSTRUCTION CO., 908 CHESTNUT ST., PHILADELPHIA, PA.

Electric generation of steam has been developed in principle and practice to a definite place in engineering work. Its main features are settled. It has been proved simple, reliable, and safe in daily operation.

It may be profitably utilized in localities where fuel cost is high and hydroelectric power is available on a low firm-power rate.

This device may well be used by central stations to consume their surplus power, and by others who have surplus power under a firm-power contract.

Among the advantages inherent in the electric steam generator are the elimination of fuel transportation, storage, and handling; elimination of ashes, smoke, or dirt; its ready adaptability to the use of surplus power; and its constant readiness for service without large standby losses. It can be located where it is most desirable and requires a minimum of attention. Long pipe lines are unnecessary when this apparatus is used.

A LARGE number of small-capacity units of various types of the electric steam generator have been in use for several years in Europe, where the high cost of fuel and the availability of hydroelectric energy offer extremely favorable conditions for such equipment. The large-capacity units, producing up to 2500 boiler h. p., such as are now in successful operation on this continent, however, are entirely due to the independent development of Mr. F. T. Kaelin, of Montreal.

While the late business depression made available a large surplus of hydroelectric power in many localities and gave cause for the installation of many large units, the actual operation of these units has proved that even where power is available only part of the day, the installation of an electric steam generator may prove a paying investment.

In fact, it is quite likely that users of hydroelectric power who are operating at less than 90 per cent load factor, and who are burning coal for steam purposes, upon investigation

will find that a definite saving may be made by the conversion of their off-peak power into steam.

The principles underlying the electric generation of steam are simple and are quite well known, but for a complete exposition of them the reader is referred to a recent paper by F. T. Kaelin.² It will be sufficient for the purpose of this short article to recapitulate them here. Steam is generated by passing alternating current directly through the water, which is heated because of its resistance to the current. Usually high-tension power is employed. The amount of heat generated by the passage of 1 kw. hr. of electric energy is equal to 3412 B. t. u. The heat content of 1 lb. of steam at, say, a pressure of 135 lbs. per sq. in., is 1193 B. t. u., and, if we assume a feed-water temperature of 150° F., the total heat to be supplied will be 1193 - (150 - 32) or 1075 B. t. u. One kw. hr., will therefore produce 3412/1075, or 3.17 lbs. of steam, no heat loss considered. On large units the heat loss is very small and the thermal efficiency can safely be taken as 98 per cent. On this basis, one kw. hr. will produce 3.10 lbs. of steam.

Under average conditions, 1 lb. of coal of about 12,000 B. t. u. evaporates 8 lbs. of water, and 1 ton, 16,000 lbs. of water. The electric energy required to evaporate the same amount of water is equal to 16,000/3.10 = 5161 kw. hr. = 215 kw. days = 0.59 kw. yrs. = 0.8 h. p. year. In short, 215 kw. in an electric steam generator are equal to 1 ton of coal per day, burned under average conditions of boiler efficiency. Since the boiler horse power is defined as the evaporation of 34.5 lbs. of water from and at 212° F. per hr. and represents 33,479 B. t. u. per hr., one kw. hr. being 3412 B. t. u. and at an average efficiency of 98 per cent equal to 3344, the relation of b. h. p. to kw. hr. is almost exactly 10 : 1, or an electric steam generator of 1000-kw. capacity is equal to a boiler of 100 b. h. p.

² "Generation of Steam by Electricity," *J. Eng. Inst. Canada*, January 19, 1922; see also F. A. Lidbury and F. A. Stamps, "An Electric Steam Generator for Low Voltage," *Trans. Am. Electrochem. Soc.*, 40 (1921), 77.

¹ Received April 5, 1922.

Electric steam generators have been built recently in sizes up to 25,000 kw., or 2500 b.h.p. The photographs show several very successful installations. The installation is inex-

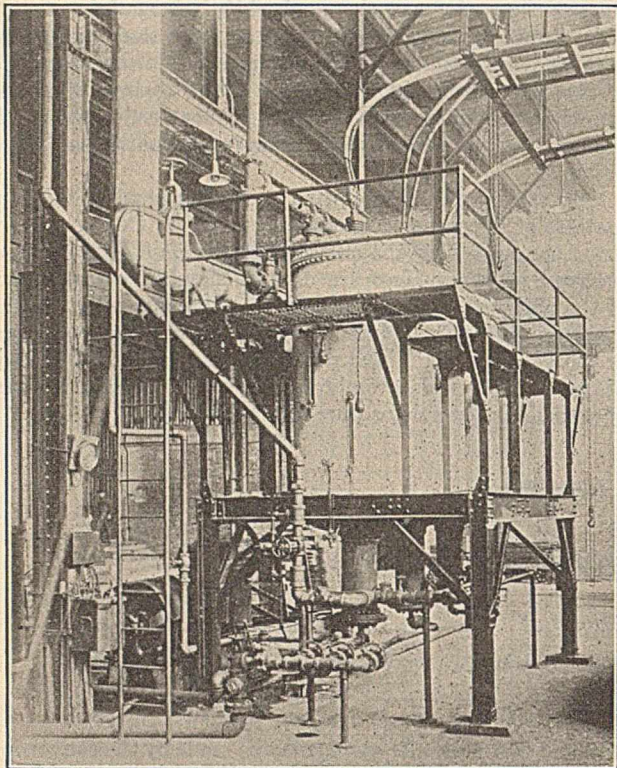


FIG 1—20,000 Kw.—2000 B. H. P. ELECTRIC STEAM GENERATOR AT PAPER MILL
Power supply—6600 volts—3 phase; pressure—135 lbs.

pensive and economical of space. About 100,000 kw. have been installed or are being built for various plants in Canada and the United States.

While the electric steam generator is of too recent development to enable us to make an authoritative forecast of its future, we can indicate certain uses and ascertain the outlines of its economic field. European practice applies this type of apparatus to the paper and pulp industries in Scandinavia, where parallel conditions with our northern states and Canada exist; to the chemical and other industries of the Rhone valley and the territory contiguous to the Alpine water powers.

Briefly, wherever abundance of hydroelectric power and high-cost fuel go hand-in-hand, the generation of steam by electricity is probably economical. Such conditions are found in the territories mentioned above and in the western United States, Brazil, Chile, and Japan.

A TEMPERATURE EXPEDIENT DURING PERIODS OF INDUSTRIAL SLACKNESS

The world is passing through a period of subnormal business activity. With demand for their output below the capacity of the plant, many mills are forced to cut costs to the last cent to survive at all. As hydroelectric power bought under a firm rate is usually contracted for in amount to take care of the plant's normal requirements, some of this is being paid for but not used when the mill is running below capacity. If coal is being burned to provide steam for drying or heating while firm power is going to waste, although paid for, the electric steam generator can be installed to use the excess power and save the cost of an equivalent amount of coal. Here it is not a question of the one method being cheaper than

the other, but one of saving good dollars and cents that are being paid out when there is already a means at hand to accomplish the purpose, even though the latter is the more expensive method under normal conditions.

Instances are on hand to prove that very often the electric steam generator can pay for itself in a few months and thereafter save the coal bill when conditions are such as outlined in the preceding paragraph. One installation saved its cost in about 2 mo., and is now helping the owner to meet the competitive conditions of the period by the saving it effects in the coal bill.

AS AN OFF-PEAK LOAD

The importance of good load-factor to power stations is undisputed and fundamental. That this is well recognized is shown by the lower rates granted by many central stations for night loads. By installing the electric steam generator to run on off-peak power, week-end power, etc., the load-factor of the system can be boosted, a very favorable rate can be made, and all parties to the contract will be benefited. In this case the steam generator will be used as auxiliary to the existing boiler capacity of the plant. There seems to be a very bright future for such applications in many hydroelectric systems.

AS A REPLACEMENT OF EXISTING PLANT, OR AS ALTERNATIVE TO NEW PLANT

In the preceding discussion, the generator has been considered without regard to the absolute relative costs of steam

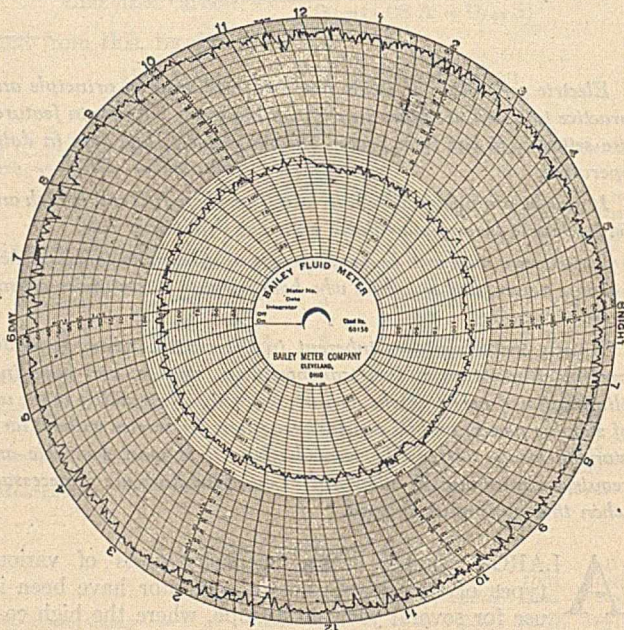


FIG. 2—BAILEY METER CHART FROM GENERATOR SHOWN IN FIG. 1, SHOWING RATE OF STEAM FLOW AND PRESSURE

produced by the two methods, but under this heading these will be included. Whenever steam is used for any purpose other than power, the fuel-burning boiler can be replaced by the electric steam generator, provided the relations of cost are in favor of the latter. The quality of steam, its pressure, and the amount are exactly the same for both methods, with the one exception that the electric generator does not deliver superheated steam. At first sight it might appear that electric power would have to be extremely cheap and coal very high indeed before serious consideration could be given to the replacement of an installation of coal boilers. On a strictly B. t. u. basis, 1 lb. of coal is equal to about 4 kw. hr., but when the relative efficiencies of application are

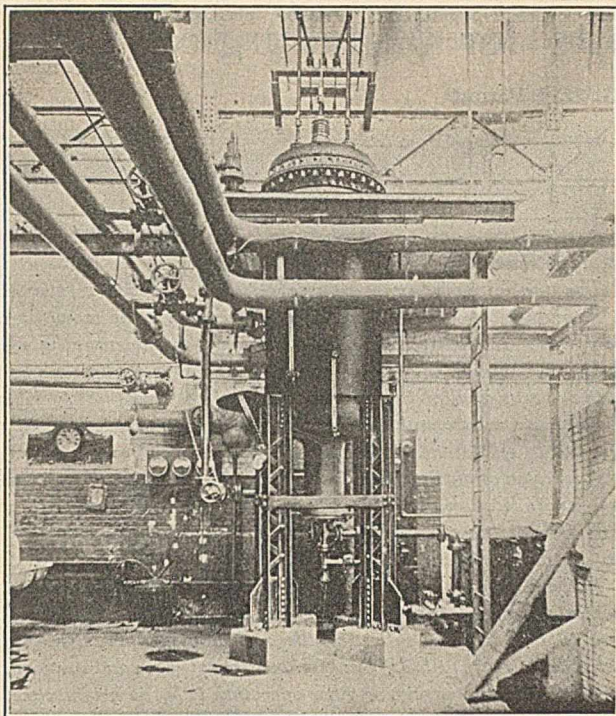


FIG. 3—5000 Kw.—500 B. H. P. ELECTRIC STEAM GENERATOR
Power supply—2200 volts—3 phase; pressure—150 lbs.

considered the difference is not so marked. If the average efficiency of small or medium-sized boiler plants is taken as 65 per cent,³ and that of the electric generator as 98 per cent, we find that 1 lb. of coal of 12,000 B. t. u. is equivalent to $2\frac{1}{3}$ kw. hr. Thus, to compete with coal at \$10.00 per ton

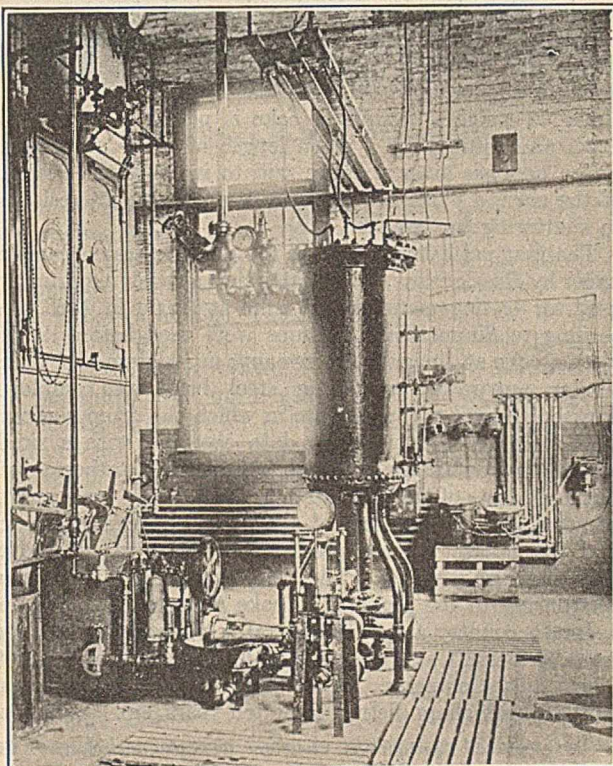


FIG. 4—1300 Kw.—130 B. H. P. ELECTRIC STEAM GENERATOR
Power supply—2200 volts—3 phase; pressure—125 lbs.

³ Fernald and Orrok, "Engineering of Power Plants," p. 158; Henry Kreisinger, "Saving Coal in Boiler Plants," *Universal Eng.*, 1919.

on the cars at the plant, on a basis of fuel cost only, electric power would have to be as cheap as 2 mills per kw. hr. The element of fuel cost is not the only one entering into the problem, however. Labor, interest on investment, and fixed charges generally will be much greater for the coal plant than for the electric generator, and in fact, aside from power cost, every item will be greater for coal plants than for the electric generator. One man can easily do all the work connected with the latter, except major repairs, for units totaling as much as 5000 b. h. p., and where the load is fairly constant, one attendant can operate a plant of twice this size.

I—COAL-FIRED PLANT⁴

(a) Cost of plant:	TOTALS
8-400 h. p. stoker-fired boilers—\$60 ⁵	\$192,000.00
Buildings and stack	40,000.00
TOTAL INVESTMENT.....	\$232,000.00

(b) Labor: ⁶	No. of Man Hours	Hourly Rate	Total Cost per Day
Number of men and duties			
1 boiler house foreman on shift.....	24	0.90	\$21.60
1 water tender on each shift..	24	0.65	15.60
1 foreman of coal handling... ..	9	0.65	5.85
2 coal handlers on each shift..	48	0.55	26.40
1 ash handler on each shift... ..	24	0.55	13.20
3 firemen on each shift.....	72	0.65	46.80
2 helpers on each shift.....	48	0.55	26.40
	249		\$155.85
Yearly cost, 365 days × \$155.85.....			\$56,885.25

(c) Fuel cost: At an average boiler and furnace efficiency of 65 per cent, the plant will burn about 60,000 tons of coal per year. Assuming this coal costs \$10 per ton in the plant, the annual coal bill will be \$600,000.00.

(d) Fixed charges (interest, depreciation, taxes, and insurance) will approximate 14 per cent,⁷ or a total yearly charge of \$32,480.00.

Combining the various items and making allowances for maintenance and supplies:

Labor.....	\$ 56,885.25
Coal.....	600,000.00
Fixed charges.....	32,480.00
Maintenance and supplies (estimated).....	6,000.00
TOTAL ANNUAL COST.....	\$695,365.25

Power for operating the coal and ash handling machinery should legitimately be charged against the cost of coal, but no account will be taken of it here.

II—ELECTRIC GENERATOR

(a) Cost of plant including necessary feed pump, hot well, etc.....	\$41,000.00
Building.....	12,000.00
(b) Labor:	\$53,000.00
1 man per shift — 60c—24 man hrs. = \$14.40 per day	
Annual labor cost, 365 × 14.40.....	\$ 5,256.00
(c) Power:	
1 b. h. p. requires approximately 13.4 e. h. p.	
3200 × 13.4 × \$15	\$643,200.00
(d) Fixed charges will be taken at 14 per cent of the investment, as in the case of the coal boiler plant	
14 per cent × 53,000.....	\$ 7,420.00
Labor.....	\$ 5,256.00
Power.....	643,200.00
Fixed charges.....	7,420.00
Maintenance.....	2,000.00
TOTAL ANNUAL COST.....	\$657,876.00

The saving in favor of the electric generator will be \$695,365.25 — \$657,876, or \$37,489.25, which sum will amortize the plant in less than 2 yrs.

⁴ Comparison of a coal-fired boiler installation and an electric steam generator in a typical paper mill. The coal plant will consist of eight 400-h. p. boilers equipped with natural draft stokers and coal and ash handling apparatus. The figures given are assumed to cover an average plant, neither the worst nor the best. Coal will be assumed to cost \$10 per ton and electric power \$15 per e. h. p. year.

⁵ Does not include piping, since this item will be approximately the same for both types of plant.

⁶ Loren E. Hibbard, *Tech. Assoc. Papers*, 4th series, p. 19.

⁷ Fernald and Orrok, *Loc. cit.*, 255; "Standard Handbook for Electrical Engineers."

The Shatter and Tumbler Tests for Metallurgical Coke^{1,2}

By S. P. Kinney³ and G. St. J. Perrott⁴

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The Bureau of Mines, in connection with its work on fuels, is conducting at the Southern Experiment Station a study of the physical properties of metallurgical coke in relation to its production and utilization. In connection with this work, a study of present testing methods has been made. This paper describes a series of experiments carried out to determine the best method of procedure and the reproducibility of duplicate determinations with (1) the machine and bag shatter tests, and (2) the tumbler or "hardness" test. Further comparative work is in progress at this laboratory and at coke plants in the district.

The shatter test affords a measure of the relative resistance of coke to breakage in handling. Single determinations by this procedure contain an average error of 1 to 3 per cent, depending on the character of the coke tested.

It is recommended that several screens be used as indicators of the shattering effect, i. e., 2-in., 1.5-in., 1-in., and 0.5-in.

Results of the bag shatter test are in fair agreement with those of the machine shatter test when the bag is dropped four times.

The effect of the size of the pieces of coke in the sample used for

the shatter test upon the absolute and relative value of the results obtained should be further studied.

The tumbler barrel or "hardness" test as at present carried out, i. e., employing 3-in. to 2-in. coke and reporting the result as the percentage remaining on a 0.25-in. screen, has no meaning when the test is applied to coke of varied physical properties. It may have value as applied to the daily testing of coke supplied to a blast furnace whose coke supply is not subject to large variations in resistance to shattering.

If a screen analysis from 2 in. to 0.25 in. be made after the tumbler test, an indication of the quality of the coke is obtained, but such data indicate no property of the coke which would not be shown by an ordinary shatter test.

If the tumbler test be carried out with 0.75- to 0.25-in. coke, the percentage remaining on a 0.25-in. or 0.17-in. screen after the test is probably indicative of the resistance to abrasion. This value, however, is little different for a variety of coke and its meaning in terms of blast furnace or other operation is by no means clear.

THE SHATTER TEST

THE SHATTER test is designed to show the resistance of coke to breakage in handling. The method and apparatus, substantially in its present form, were developed some years ago by D. T. Croxton and have been described by Belden.⁵ Fig. 1 shows the machine shatter test apparatus in use at this Station. It was built in accordance with tentative specifications formulated by Committee D-6 on Coke, from a blue-print supplied through the courtesy of the Koppers Company.

In the test procedure, a 50-lb. sample of coke is dropped four times from a height of 6 ft. upon a steel plate. The percentage of the original sample, which remains on a 2-in. square mesh screen after this treatment, is reported as the shatter test result.

An alternative method of conducting the shatter test has been proposed by C. R. Meissner of the Koppers Company. In this method the procedure is identical, except that the coke is placed in a heavy sulfate bag about 45 in. long by 28 in. wide and rolled from a shelf 6 ft. above a concrete floor or steel plate. Figs. 2 and 3 show a modification of the bag shatter test used in our work.

Examination of the test procedure shows need for consideration of the following points:

- 1—Weight of sample to be employed.
- 2—Method of sampling and size of coke pieces to be taken.
- 3—Mesh of screen used as indicator of the shattering effect and method of conducting the screening.
- 4—Agreement obtainable between results of duplicate determinations.

¹ Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² Published with permission of the Director, U. S. Bureau of Mines.

³ Assistant Metallurgical Chemist, Southern Experiment Station, U. S. Bureau of Mines.

⁴ Associate Physical Chemist, Southern Experiment Station, U. S. Bureau of Mines.

⁵ "Metallurgical Coke," *Bur. Mines, Tech. Paper* 50 (1913), 39.

THE TUMBLER BARREL TEST

After the coke is discharged into the bell of the blast furnace it is no longer subject to breakage by impact. The action is then one of slow abrasion as the coke travels down the furnace under the increasing weight of the burden above. A number of workers have developed tests designed to give a relative value for the resistance of coke to mechanical attrition in the furnace. Although there is considerable variation in test procedure, all the methods are the same in principle. A weighed sample of coke is placed in a revolving drum and rotated for a given length of time. Subsequent screen analysis gives a figure said to indicate the friability of the coke, a value not necessarily related to its resistance to shattering by impact.

The first published record of the tumbler test occurs in a paper by Rossignaux,⁶ who states that a revolving drum was used for testing metallurgical coke at Anzin in 1883. According to Simmersbach,⁷ drums were used before 1904 for testing coke at Jurjewka, Germany; in Belgium and France similar apparatus containing steel balls was employed. Hewson⁸ describes a procedure in which the drum contained steel balls. Cochrane⁹ gives data obtained with a similar apparatus containing no steel balls. This author carried out daily tests of the coke used by his furnaces for a number of years and claimed to find a relation between test results and the amount of iron produced by his furnaces and the blast pressure required. The English workers gave the name "hardness" to the property of coke measured by their test.

In this country a similar apparatus has been used for some time by Barrett at Youngstown and by Rice¹⁰ of the Bethlehem Steel Company. A similar "rumbler" test was in use in the Birmingham district some ten years ago. Rice, using

⁶ "Propriétés Physiques et Chimique du Coke Metallurgique," *Génie civil*, 20 (1891), 9, 21.

⁷ *Stahl u. Eisen*, 33 (1913), 512.

⁸ *J. Soc. Chem. Ind.*, 37 (1918), 60.

⁹ *J. Iron Steel Inst.*, 97 (1918), 141.

¹⁰ "Importance of Hardness of Blast Furnace Coke," *Am. Inst. Mining Met. Eng.*, Preprint No. 1030 (1921).

an apparatus containing steel balls, found that over a period of months a low hardness number went hand-in-hand with high blast pressure required to blow a given volume of air through the furnace.

Examination of the test procedure shows need for consideration of the following points:

- 1—Weight of sample to be employed.
- 2—Method of sampling and size of coke pieces to be taken.
- 3—Mesh of screen used as indicator.
- 4—Agreement obtainable between results of duplicate determinations.
- 5—Duration of test.

COKE SAMPLES TESTED

The greater part of the work has been carried out on samples of coke from the Birmingham district. Tests have also been made on beehive coke from the Connellsville district, on by-product coke from Benham coal, and on by-product coke from Illinois coal.

TABLE I—DESCRIPTION OF COKE SAMPLES

NAME	TYPE OF OVEN	COKING TIME HRS.	COAL SEAM
Alabama:			
No. 1	Koppers	17	{ 66% Black Creek
No. 2	Beehive	72	{ 34% Mary Lee
No. 3	Semet-Solvay	20	Milldale
No. 4	Beehive	72	Mary Lee
No. 5	Semet-Solvay	16	Brookwood
No. 6	Beehive	72	Brookwood & Milldale
No. 7	Beehive	72	Pratt
No. 8	Semet-Solvay	34	Mary Lee
No. 9	Koppers	19	Mary Lee
No. 10	Koppers	20	Pratt
No. 11	Beehive	72	Blue Creek
Benham	Wilputte	29	{ 92.5% Keokee
Connellsville	Beehive	72	{ 7.5% Pocahontas
Illinois	Roberts	15	No. 7
Pitch coke	Beehive	72

TABLE II—ANALYSIS OF COKE SAMPLES

COKE	PROXIMATE				ULTIMATE						
	Mois- Vola- ture	tile	F. C.	Ash	H	C	N	O	S	B. t. u.	
Alabama:											
No. 1	1.53	3.17	84.75	10.55	1.42	84.00	1.60	1.52	0.74	12718	
No. 2	0.20	0.90	88.57	10.33	0.56	86.79	0.65	0.80	0.85	12624	
No. 3	0.18	1.07	84.92	13.83	0.47	83.59	0.72	0.57	
No. 4	0.50	1.35	86.62	11.53	0.53	85.72	0.82	0.47	0.87	12473	
No. 5	0.8	1.4	87.10	10.70	0.80	85.0	1.3	1.2	1.0	12690	
No. 6	2.39	1.03	85.5	11.06	1.27	12389	
No. 7	0.40	0.48	84.37	14.75	0.78	12139	
No. 8	3.02	2.92	81.30	12.76	0.70	84.21	1.19	0.88	0.72	12079	
No. 9	0.25	1.15	90.70	7.90	0.52	89.16	0.96	0.33	1.11	13044	
No. 10	0.50	2.68	87.74	9.08	0.84	87.14	0.74	1.04	1.10	12929	
No. 11	0.28	0.57	87.97	11.18	0.31	86.73	0.95	0.00	0.80	12452	
Benham	0.9	0.9	91.7	6.5	0.7	13330	
Connellsville	0.48	1.77	86.00	11.75	0.79	84.35	1.22	0.86	0.97	12527	
Illinois	1.3	1.4	86.0	11.3	0.3	86.2	0.4	0.8	0.9	12450	
Pitch coke	0.33	1.07	97.65	0.95	0.55	96.66	0.72	0.62	0.50	14097	

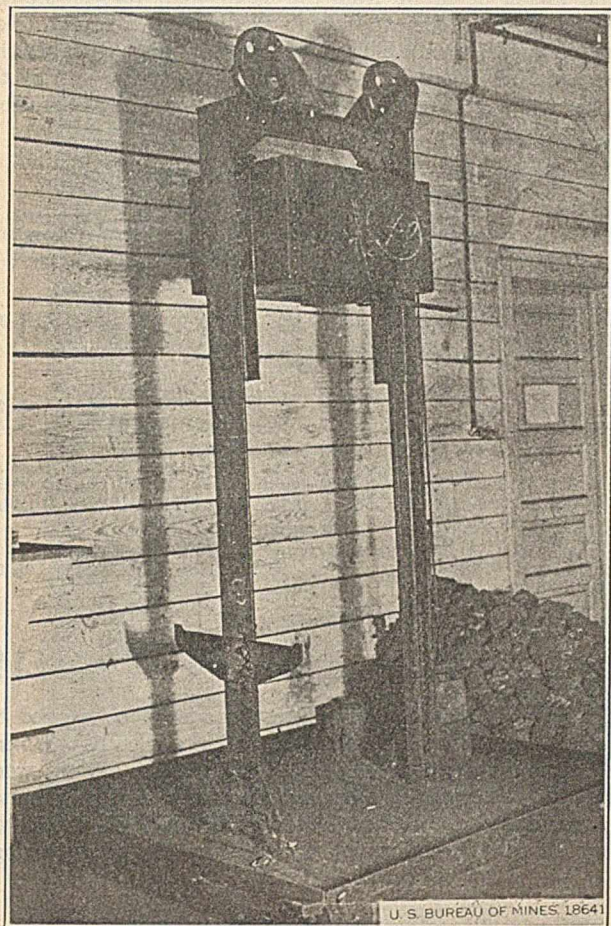


FIG. 1—MACHINE SHATTER TEST APPARATUS

Drums from 2 to 6 ft. in diameter have been employed, and coke samples of 25 to 900 lbs.

The tumbler test apparatus used at this laboratory is substantially the same as described by Cochrane.⁹ The machine, shown in Figs. 4 and 5, consists of a steel drum of 0.25-in. boiler plate, 30 in. in inside diameter and 18 in. in length. The drum is rotated by means of a motor connected to a standard pitch worm gear at the rate of 18.6 r. p. m. The current to the motor is automatically interrupted after the drum has made 1200 revolutions. The machine is set in the top of a bin. The bin discharges on to a set of circular screens 2 ft. in diameter and having the following square openings between wires: 2-in., 1.5-in., 1-in., 0.5-in., and 0.25-in.

A 25-lb. sample of 3- to 2-in. coke is placed in the apparatus for the test, the cover fastened down, and the drum revolved 1200 times. In the subsequent screen analysis, the screens are shaken and the pieces tested separately to see whether they will pass the openings in any position. This procedure gives a more definite end-point than any method of shaking. The so-called hardness number is reported as the cumulative percentage of the original sample remaining on the 0.25-in. screen. As data were desired on the choice of screens to be used for determining the hardness number, a greater number of screens were used than employed by Cochrane.

Table I shows the character of the coke samples tested. Table II gives proximate and ultimate analyses of the cokes. Table III summarizes data obtained on physical properties of the coke samples. True density was determined on material ground to pass a 200-mesh screen. Apparent density was determined on 1.75-in. material by a method measuring the volume of water displaced by a weighed amount of the coke.

DETAILED DATA OF MACHINE AND BAG SHATTER TEST DETERMINATIONS

To determine the agreement obtainable between the results of the machine and bag shatter tests and the agreement obtainable between duplicate determinations by each method, a series of tests was run on two by-product cokes made in Alabama. Part of these tests were carried out at the laboratory and part were run at the plant. Sufficient coke to run from five to ten tests was taken at one time and well mixed on the floor before the shatter tests were made. The purpose of the tests was not so much to get a representative sample of the coke contained in the bin or larry car as to secure a large well-mixed pile of coke from which identical samples might be taken.

TABLE III—PHYSICAL PROPERTIES OF COKE SAMPLES

COKE	SHATTER	HARDNESS		SPECIFIC GRAVITY		POROSITY
		A ¹	B ²	True	Apparent	
Alabama:						
No. 1	70	70	...	1.75	0.96	45
No. 2	74	73	89.1	2.10	1.02	52
No. 3	69	68	89.4	1.96	1.00	49
No. 4	72	67	...	1.91	0.83	57
No. 5	69	71	90.6	2.00	0.99	51
No. 6	64	74	90.2	2.13	1.15	46
No. 7	72	71	88.8	1.91	0.98	49
No. 8	70	74	90.4	1.98	1.05	47
No. 9	70	74	92.3	2.04	1.14	44
No. 10	70	68	...	1.92	0.98	49
No. 11	77	73	...	1.97	0.81	59
Benham	59	73	88.4	1.85	0.91	51
CConnellsville	66	71	92.0	1.89	1.02	46
Illinois	42	78	90.5	1.84	0.87	53
Pitch coke	78	76	92.9	2.00	1.16	42

¹ Method using 3- to 2-in. coke; result reported as percentage remaining on a 0.25-in. screen.
² Method using 0.75- to 0.25-in. coke; result reported as percentage remaining on a 0.17-in. screen

Table V shows the difficulty of drawing conclusions from a single shatter test determination. The table gives condensed data from the daily shatter test records of a by-product plant. One shatter test is made each day at this plant under normal conditions. Daily results show a somewhat higher deviation from the mean value for the month than is shown in the experiments run by the writers on coke from a single oven. This indicates that there is probably some real difference in the quality of the coke from day to day, but the difference is evidently too small to be detected by a single determination.

TABLE VI—MACHINE SHATTER TESTS WITH SIZED COKE

On Screen analysis after test, cumulative per cent	Through 3-in. on 2-in. screen				Through 5-in. on 3-in. screen			
	Ala. No. 8 (Av. of 18 tests) (150 pieces in 50-lb. sample)	Ala. No. 5 (Av. of 9 tests) (170 pieces in 50-lb. sample)	Ala. No. 8 (Av. of 9 tests) (47 pieces in 50-lb. sample)	Ala. No. 5 (Av. of 9 tests) (60 pieces in 50-lb. sample)	Ala. No. 8 (Av. of 9 tests) (47 pieces in 50-lb. sample)	Ala. No. 5 (Av. of 9 tests) (60 pieces in 50-lb. sample)	Ala. No. 8 (Av. of 9 tests) (47 pieces in 50-lb. sample)	Ala. No. 5 (Av. of 9 tests) (60 pieces in 50-lb. sample)
	2-in.	1.5-in.	1-in.	0.5-in.	2-in.	1.5-in.	1-in.	0.5-in.
75.3	91.2	95.9	98.7	74.3	90.1	95.3	98.2	
Deviation of single determination from mean:								
Average	±2.1	1.1	0.8	.4	1.7	0.8	0.5	0.7
Maximum	±9.8	2.9	1.5	1.0	2.3	2.5	1.4	1.5
	Through 5-in. on 3-in. screen							
	2-in.	1.5-in.	1-in.	0.5-in.	2-in.	1.5-in.	1-in.	0.5-in.
75.8	86.1	92.8	96.2	71.8	86.0	94.0	98.0	
Deviation of single determination from mean:								
Average	±1.8	1.1	0.8	1.2	0.9	1.3	0.7	0.6
Maximum	±3.8	2.5	1.5	2.6	1.8	2.6	1.2	2.2

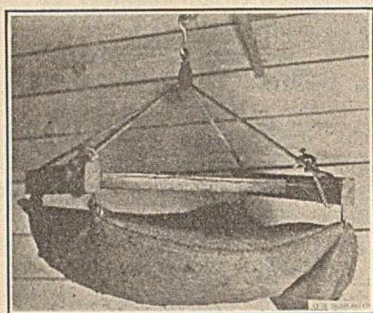


FIG. 2—BAG SHATTER TEST APPARATUS

Table IV gives a condensed record of the tests made with both machine and bag shatter procedure. Conclusions to be drawn from the data are as follows:

- 1—Single determinations by the shatter test procedure contain an average error of 1 to 3 per cent depending on the character of the coke. Several duplicate determinations should be made.
- 2—Results of bag and machine shatter tests are in fair agreement.
- 3—A lower shatter test value is obtained when full length pieces of coke are used than when a run-of-oven sample is taken.
- 4—Stock coke at the Semet-Solvay plant has not deteriorated in strength as measured by the shatter test.

TABLE IV—SUMMARY OF SHATTER TEST RESULTS

COKE	Coking Hrs.	Size Coke Used	Type of Test	No. of Determinations	Mean Value Per cent on 2-in. Screen	DEVIATION FROM MEAN		WHERE TESTED
						Average	Max.	
Alabama: No. 8	34	F. L.	M	5	71.8	±1.0	±2.2	Bureau of Mines Station
	34	F. L.	B	10	68.9	3.3	12.9	
	34	R. O.	M	13	76.3	3.0	12.3	
	34	R. O.	B	17	77.3	2.0	5.7	
Alabama: No. 5	16	F. L.	M	9	71.8	0.9	1.8	At plant
	16	R. O.	M	10	69.6	2.7	6.6	
			B	8	67.1	1.7	4.6	
	15.5	R. O.	M	25	61.9	2.1	8.1	
			B	23	63.3	1.5	4.8	
	15.5	R. O.	M	21	63.5	1.9	6.0	
		B	25	64.1	1.8	4.8		
	16.5	R. O.	M	26	62.5	1.3	4.0	
	16.5	R. O.	M	23	65.1	0.8	2.6	
	25	R. O.	M	24	65.0	1.1	4.0	
Alabama No. 5:								
Stock coke ¹	24	R. O.	M	10	67.4	1.3	2.9	
Stock coke ²	..	R. O.	M	10	66.1	0.9	2.1	

F. L. indicates that pieces of coke about half the width of the oven were used for the test.
 R. O. indicates that run-of-oven coke screened over a 2-in. screen was used for the test.
¹ In stock pile for one year.
² In stock pile for two years.

TABLE V—DAILY SHATTER TEST DATA AT BY-PRODUCT PLANT (ALABAMA NO. 5)

Month 1921-22	Number of Tests	Mean Monthly Shatter Test Value	DEVIATION OF DAILY RESULTS FROM MEAN	
			Average	Maximum
October	15	63.3	±2.7	±7.3
November	23	67.6	3.0	9.6
December	27	68.3	2.4	7.7
January	20	66.5	2.5	6.5
February	20	66.2	3.4	9.8
March	10	67.0	1.4	3.0

Table VI shows a series of tests made on coke sized to pass a 3-in. and remain on a 2-in. screen and to pass a 5-in. and remain on a 3-in. screen. These determinations were made in the hope of securing more reproducible results, on account of the increased number of pieces in the 50-lb. sample and the uniformity obtained by the closer sizing.

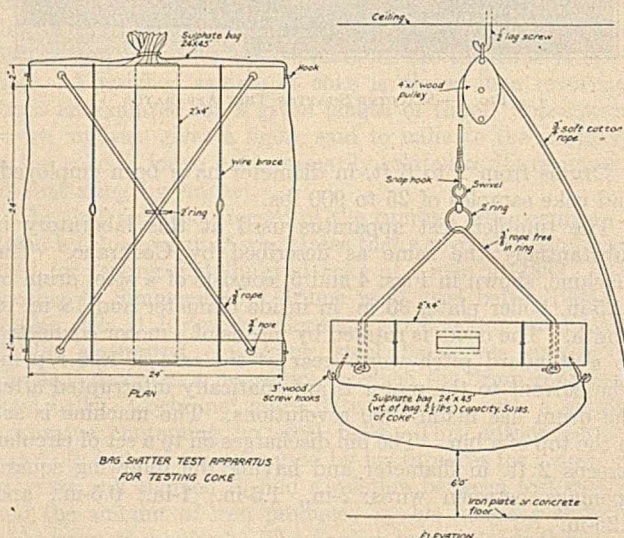


FIG. 3

Results indicate somewhat better reproducibility. The interesting development from these tests lay in the data obtained when the material passing a 2-in. screen after the shatter test was subjected to further screen analysis. It will be seen that whereas Cokes 8 and 5 show 76 per cent and 72 per cent, respectively, on the 2-in. screen, the value on the 1.5-in. screen, 86 per cent, is identical for the two cokes. When the 0.5-in. screen is used as the indicator of the shattering effect, we find that 96 per cent of Coke 8 remained on

the screen as against 98 per cent of Coke 5. The producer of Coke 5, on being reproached for the inferiority of his product, might well point out that screening on a 2-in. screen

TABLE VII—COMPARISON OF SHATTER TEST RESULTS WHEN FOUR SCREENS ARE EMPLOYED

COKE	Screen Analysis after Test, Cumulative Per cent			
	On 2-in.	1.5-in.	1-in.	0.5-in.
Alabama No. 8	75.8	86.1	92.8	96.2
Alabama No. 5	71.8	86.0	94.0	98.0
Benham	59.0	72.5	83.7	94.9
Illinois	41.6	62.0	81.2	96.0

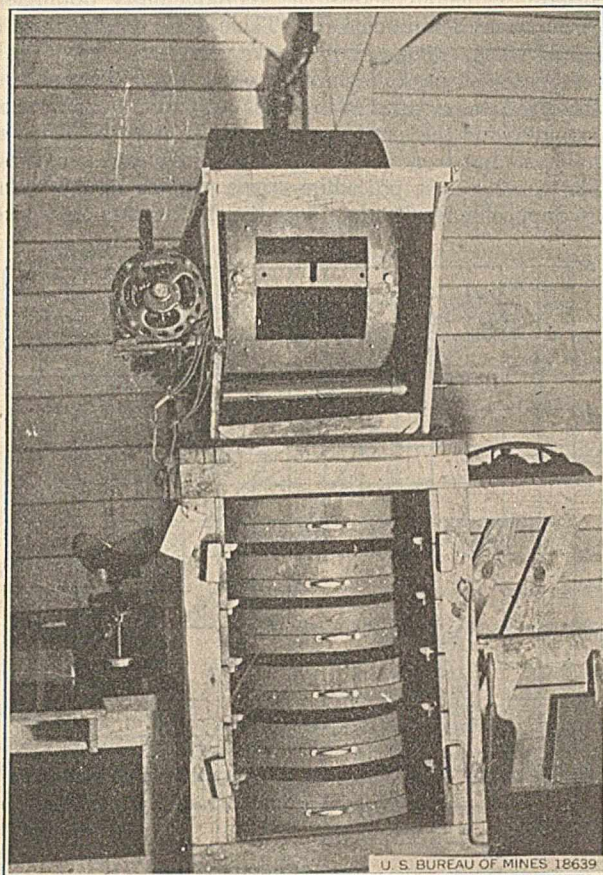


FIG. 4—TUMBLER TEST APPARATUS

is a more or less empirical procedure and that his coke showed less material passing the 0.5-in. screen than did Coke 8. It is therefore believed desirable to use a number of screens as indicators of the resistance to shattering.

Table VII compares shatter test results on four coke where the material after the test has been subjected to screen analysis. This table indicates the desirability of using the four screens, for it shows that Cokes 8 and 5 differ little in resis-

tance to shattering, while the Benham and Illinois coke are more fragile, whatever screen is employed as indicator.

It is not believed advisable to change the design of the present apparatus, although more reproducible results would no doubt be obtained if a larger apparatus and correspondingly larger sample of coke were employed. From two to five duplicate determinations (the number depending on the variation between duplicate test results with the coke in question) should be made.

We desire a value from the shatter test procedure which will show the intrinsic merit of the coke, a value by which coke varying widely in physical characteristics may be compared. From our data it is evident that attention should be paid to the size of coke pieces taken. For example, the shatter test value on Coke 8 was 72 per cent when pieces half the width of the oven were used and 76 per cent when run-of-oven coke was used. If the run-of-oven coke had been handled more before the test, this result might have been still higher.

The size and number of the large or "full length" pieces vary considerably between different plants. The advisability of employing a standard size should be considered. For the present, lacking the large amount of data necessary to determine the effect of sizing on the absolute and relative value of the shatter test result, it is recommended that large pieces about half the width of the oven be employed. With beehive coke, pieces 7 to 10 in. in length should be used, the sample being obtained as recommended in the tentative specifications of Committee D-6.

In screening the coke after the shatter test, it has been found best to put through the screen all pieces which will go through in any position. This procedure has given a better reproducible value than any method of shaking.

DETAILED DATA OF TUMBLER TEST DETERMINATIONS

The large samples of coke used for shatter test determinations were employed in making the tumbler tests. In the tentative specifications of the A. S. T. M., coke for the test is sized to pass a 3-in. and remain on a 2-in. square mesh screen. Owing to the difficulty experienced with Coke 8 in duplicating results when this size coke was employed,

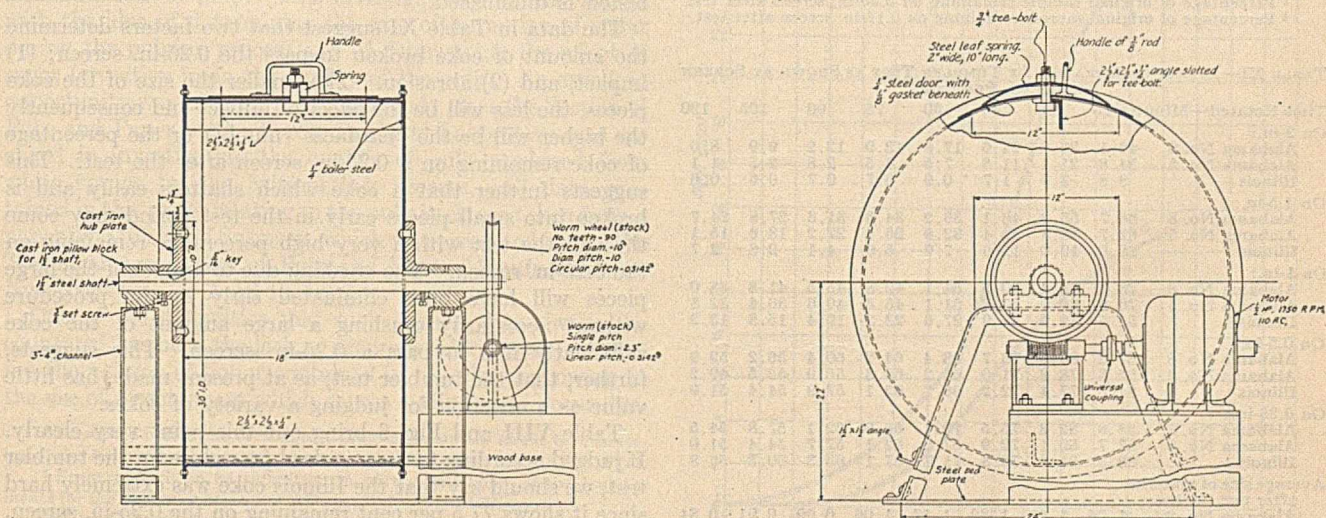


FIG. 5

a series of tests was made with various sizes of coke. A number of experiments were made to investigate the possibility of decreasing the time required for the test.

Groups of five to fifteen samples were prepared at the same time. Large pieces were broken to pass the 3-in. screen and remain on the screen chosen for the lower limit. The sample was well mixed and 25-lb. portions were weighed out for the tests.

TABLE VIII—SUMMARY OF TUMBLER TEST DATA

COKE	No. of Determinations	Screen Analysis after Test, Accumulative Per cent on Screen					Av. Diameter of Coke Pieces after Test, In.	REMARKS
		2-in.	1.5-in.	1-in.	0.5-in.	0.25-in.		
Alabama:								
No. 1	2	12.7	42.0	57.4	69.9	70.1	1.15	
No. 2	2	10.0	40.0	56.5	71.0	73.0	1.14	
No. 3	2	15.1	36.1	51.2	65.6	68.1	1.10	
No. 4	2	12.8	38.6	54.2	66.1	67.0	1.10	
No. 5a	5	12.2	38.6	58.8	72.5	74.7	1.15	16.5-hr. coke
No. 5b	10	12.3	34.9	53.1	68.7	72.5	1.10	16-hr. coke
No. 1c	8	10.6	36.8	55.2	68.6	70.7	1.09	15.5-hr. coke
No. 5d	5	18.1	34.4	58.6	65.7	67.6	1.14	24-hr. coke, in stock 1 year
No. 5e	5	21.5	43.3	57.7	69.5	71.1	1.24	25-hr. coke
No. 6	3	10.2	37.0	53.7	71.2	73.6	1.10	
No. 7	3	14.5	45.1	59.4	70.0	71.4	1.21	
No. 8	2	19.2	43.2	59.1	72.2	73.6	1.24	
No. 9	3	14.3	38.8	57.3	71.3	73.6	1.17	
No. 10	4	14.9	38.9	54.0	66.8	67.9	1.12	
No. 11	2	18.2	51.9	61.4	65.6	73.0	1.25	
Benham	5	11.0	25.4	41.8	69.2	72.8	0.99	
Cornellsville	3	18.1	39.2	52.8	68.5	70.6	1.16	
Illinois	8	2.6	12.3	33.6	72.5	77.5	0.85	
Pitch coke	3	37.6	71.1	75.1	75.3	75.6	1.16	

TABLE IX—REPRODUCIBILITY OF TUMBLER TEST DETERMINATIONS

COKE	No. of Determinations	Mean "Hardness" No. ¹	Deviation of Single Determinations from Mean	
			Average	Maximum
Alabama No. 8	13	73.5	±1.2	±2.5
Alabama No. 5	18	70.7	0.4	0.9
Benham	5	72.8	0.9	2.3
Illinois	8	77.5	0.6	2.0

¹ Percentage of original sample remaining on 0.25-in. screen after test.

TABLE X—TUMBLER TESTS WITH VARIOUS SIZES OF COKE

SIZE OF COKE Through On	No. OF TESTS		Mean Value	"HARDNESS" NUMBER ¹		Mean Value	Deviation of Single Determinations from Mean	
	Ala.	No. 8		Ala.	Ala. No. 5		Av.	Max.
3-in.	25	5	79.2	±2.3	±7.7	73.4	±0.6	±1.5
3	6	5	78.5	1.1	3.4	72.5	0.4	0.6
3	1.5	5	75.6	0.9	1.6	73.6	1.5	3.3
3	2	13	73.5	1.2	2.5	70.7	0.3	0.9
3	2.5	6	75.7	3.0	7.5
2.5	3	3	76.7	0.9	1.5
2	1	5	77.2	0.5	1.5
2	0.5	25	79.6	1.2	2.0	77.0	0.8	1.4
1.5	0.5	5	81.6	1.2	2.6
0.75	0.25	5	90.4 ²	0.5	1.2	90.6 ²	0.3	0.9

¹ Percentage of original sample remaining on 0.25-in. screen after test.

² Percentage of original sample remaining on 0.17-in. screen after test.

TABLE XI—EFFECT OF DURATION OF TUMBLER TEST AS SHOWN BY SCREEN ANALYSIS, PER CENT

Time Rotated—Minutes	ANALYSIS, PER CENT							
	15	30	45	60	75	90	105	120
On 2-in.:								
Alabama No. 8	46.1	33.8	24.6	17.8	13.9	12.2	9.9	8.6
Alabama No. 5	34.8	21.1	11.8	7.5	4.5	2.8	2.8	1.1
Illinois	8.8	3.9	1.7	0.9	0.7	0.7	0.6	0.6
On 1.5-in.:								
Alabama No. 8	66.7	55.2	46.1	39.2	34.5	31.3	27.8	24.7
Alabama No. 5	62.7	48.8	39.4	32.9	26.4	22.2	18.6	15.1
Illinois	28.6	19.0	12.6	7.9	5.6	4.1	2.8	2.7
On 1-in.:								
Alabama No. 8	78.4	68.4	60.5	54.1	49.8	45.5	41.8	38.0
Alabama No. 5	76.9	66.0	57.8	51.1	45.5	40.6	36.4	32.8
Illinois	54.5	42.9	33.9	27.6	23.2	19.4	15.8	13.2
On 0.5-in.:								
Alabama No. 8	87.2	80.5	73.7	68.4	64.2	60.4	56.2	52.9
Alabama No. 5	85.8	78.2	71.0	65.2	60.3	55.9	52.5	49.2
Illinois	84.5	77.4	72.2	66.7	62.1	57.9	54.4	51.9
On 0.25-in.:								
Alabama No. 8	88.8	82.3	75.5	70.1	66.0	62.1	57.8	54.5
Alabama No. 5	87.7	80.1	72.9	67.0	62.1	57.7	54.4	51.0
Illinois	88.3	81.8	76.8	71.7	67.1	63.3	60.3	56.8
Average size of material after test, inches:								
Alabama No. 8	1.75	1.51	1.32	1.17	1.06	0.99	0.91	0.84
Alabama No. 5	1.64	1.37	1.15	1.02	0.90	0.81	0.76	0.69
Illinois	1.14	0.96	0.85	0.74	0.68	0.63	0.58	0.56

Table VIII summarizes results obtained with the standard procedure, using 3- to 2-in. coke. Figures in the column headed "0.25-in." give the "hardness number" as usually reported. Table IX shows the reproducibility obtainable with duplicate determinations. Table X summarizes results obtained when various sizes of coke were employed. Table XI shows the effect of the duration of the test. The rotation of the drum was stopped at intervals of 15 min. over a period of 120 min. and the usual screen analysis made. The entire sample was put back in the apparatus after each screening.

The tumbler test procedure seems capable of producing more duplicable results than does the shatter test procedure,

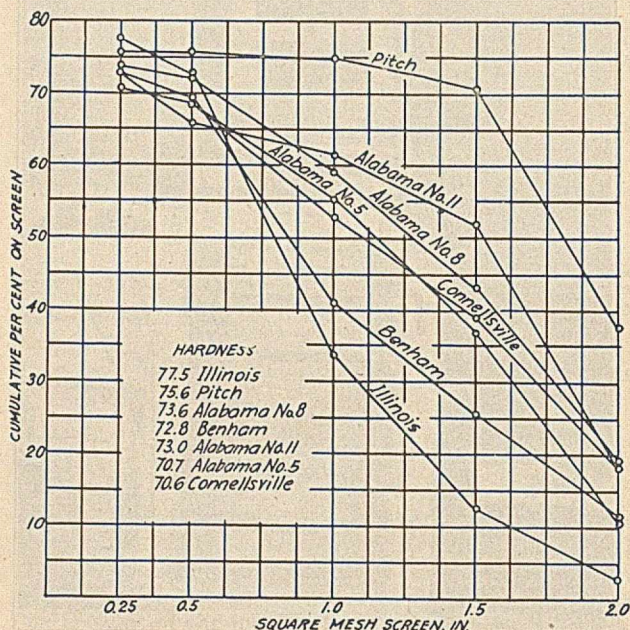


FIG. 6—SCREEN ANALYSIS OF COKES AFTER TUMBLER BARREL TEST

the result probably of smaller and closer sizing of the sample and the duplicable mechanical nature of the test.

As seen from Table XI reducing the upper size limit (1) gives somewhat more reproducible results with Coke 8 but does not increase the reproducibility with Coke 5; (2) gives results for the two cokes which show a decreasing difference until the 0.75- to 0.25-in. size is reached, where results for both cokes are practically identical; and (3) gives results whose values are increasingly higher as the size of the material tested is diminished.

The data in Table XI suggest that two factors determine the amount of coke broken to pass the 0.25-in. screen: (1) impact, and (2) abrasion. The smaller the size of the coke pieces, the less will be the effect of impact and consequently the higher will be the "hardness" number or the percentage of coke remaining on a 0.25-in. screen. This suggests further that a coke which shatters easily and is broken into small pieces early in the test period may come through the test with a very high percentage remaining on the 0.25-in. screen. The crushing due to impact of the large pieces will have been eliminated early in the procedure without necessarily crushing a large amount of the coke sufficiently fine to pass a 0.25-in. screen. This suggests, further, that the tumbler test, as at present made, has little value as a criterion for judging a variety of cokes.

Table VIII and Fig. 6 bring out this point very clearly. If judged according to the standard procedure for the tumbler test, we should say that the Illinois coke was extremely hard since it shows 77.5 per cent remaining on the 0.25-in. screen. However, we note that only 15 per cent of the Illinois coke

was larger than 1.5 in. after the test, as against 36 to 60 per cent of the other cokes. As shown by the interval tests in Table XI, the Illinois coke broke up much more rapidly during the first 15 min. The "average size" figures in Tables VIII and XI were calculated for the purpose of indicating by a single value the result of the screen analysis.¹¹

Comparison with the shatter test data makes it appear doubtful whether the screen analyses of the tumbler test

¹¹ Specimen calculation of average size.

BENHAM COKE					
Per cent on Screen		Av. Diameter, In.			
2-in.	11.0	×	2.5	=	0.28
1.5-in.	14.4	×	1.75	=	0.25
1-in.	16.4	×	1.25	=	0.21
0.5-in.	27.4	×	0.75	=	0.21
0.25-in.	3.6	×	0.38	=	0.01
0.25-in.	27.2	×	0.13	=	0.03
AVERAGE DIAMETER					0.99 in.

material show any property of the coke not indicated by the shatter test. Certainly the test as at present made and reported as the percentage remaining on the 0.25-in. screen has little meaning when applied to cokes of varied physical properties.

If the abrasive factor alone is to be considered, it would seem best to use small-sized coke, *e. g.*, 0.75- to 0.25-in., and to eliminate the baffles in the apparatus. The variation in this value between the cokes tested is not large, as seen in Table III, and it is doubtful whether it has a meaning in terms of blast furnace or other operation.

ACKNOWLEDGMENT

This investigation was conducted under the direction of A. C. Fieldner, Supervising Fuels Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, in cooperation with Committee D-6 on Coke of the American Society for Testing Materials.

Sugar Formation in a Sulfite Digester^{1,2,3}

By E. C. Sherrard⁴ and C. F. Suhm

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The results of the following investigation indicate that the rate of sugar formation is influenced chiefly by the temperature and concentration of free sulfur dioxide. Time is also a factor since prolonged cooking increases the sugar production but at the expense of the cellulose.

IN A PREVIOUS paper⁵ on the manufacture of ethyl alcohol from waste sulfite liquor the desirability of investigating the rate of sugar formation in the digester was pointed out. It is known that in commercial practice a marked fluctuation occurs in the sugar content of waste sulfite liquor, a condition that is highly detrimental to the alcohol process. This variation seems to be influenced by concentration of raw acid, the sugar content of the liquor varying between 1.94 and 2.80 per cent in winter, and between 1.65 and 2.20 per cent in summer. For the ethyl alcohol process to be commercially profitable it is necessary at all times to obtain the maximum quantity of sugar with a minimum loss of pulp. This investigation was undertaken with the idea of determining the rate of formation of sugar during the pulping process and of determining the effect of sugar formation upon the quality of the pulp. An excellent opportunity was afforded for such a study since the Section of Pulp and Paper of the Forest Products Laboratory was engaged in investigating the quality of pulp produced from white spruce by the Mitscherlich process. All data contained in this paper relating to the pulp itself are taken from a paper by Miller and Swansen, which was presented before the Technical Association of Pulp and Paper Manufacturers in New York City on April 10, 1922.

One of the difficulties that such a study has always encountered has been the lack of accurate information concerning the volume of liquor contained in the digester, owing to the use of direct steam which causes a dilution to occur dur-

ing the digestion. It has also been difficult to obtain accurate samples from the blow pit because of dilution by the wash water. In this case accurate data were obtained in each cook as to the dry weight of the wood used and the quantity of liquor in the digester at the time of sampling. All of these cooks were carried out on white spruce wood in an experimental digester having a capacity of 50 lbs. of pulp.

Sugar determinations were made by means of Fehling's solution, with subsequent electrolytic deposition of the copper at intervals of 1 or 2 hrs., during the progress of 8 cooks in which the conditions such as the concentration of sulfur diox-

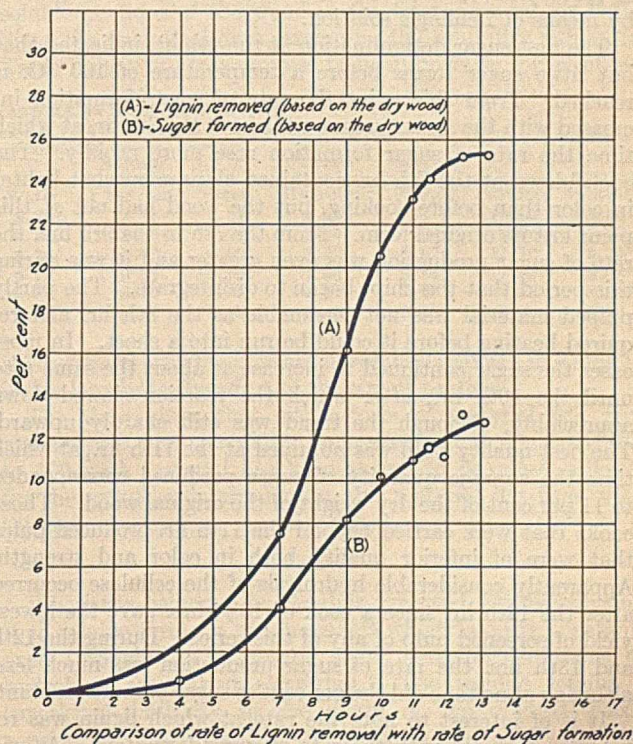


FIG. 1

¹ Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² From a thesis to be submitted in partial fulfillment of the requirements for the degree of Master of Science, University of Wisconsin.

³ Published with permission of the Department of Agriculture.

⁴ Chemist, Forest Products Laboratory, Madison, Wis.

⁵ Sherrard and Blanco, *Paper*, 24, No. 17 (1919), 746.

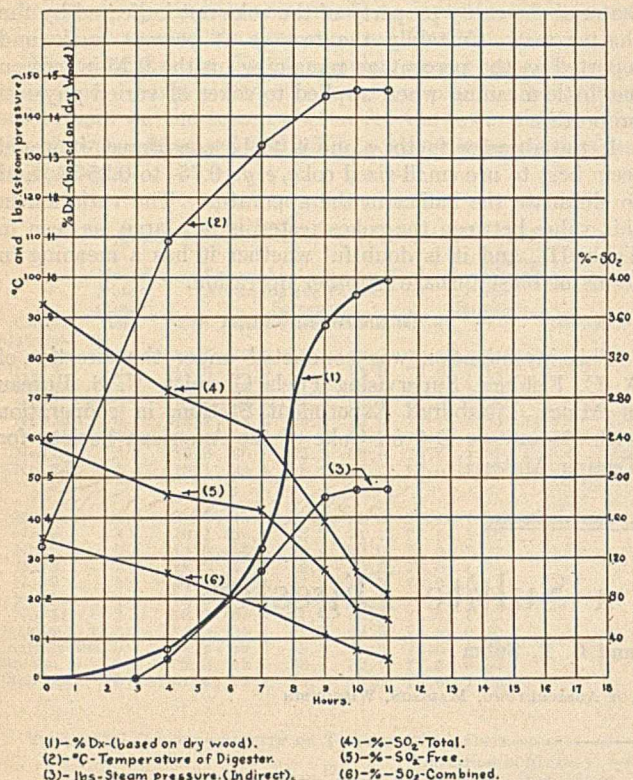


FIG. 2

ide—total, free, and combined—temperature, and pressure were held as nearly constant as possible. These cooks were blown after different periods of time in order to study the progress of the reaction in respect to the quality of the pulp and the quantity of total reducing sugar. The average per cent of total reducing sugar for all cooks at a given hour is plotted against time in Fig. 1. The total sugar is designated as glucose (Dx), since it was determined in terms of glucose by means of Fehling's solution.

The first sugar determination at the 4th hr. indicated that but little sugar forms before a temperature of 100° C. is reached. From this point the rate of sugar formation increased with the steam pressure to about the 7th hr. at which time the rate of sugar formation rose more rapidly. The cook blown at the 7th hr. contained chips somewhat lighter in color than before cooking, but the wood had not at this point lost its original form. From the 7th to the 9th hrs. the rate of sugar production was even greater and it was during this period that the chips began to disintegrate. The partly pulped material was not screenable at the 9th hr. and required beating before it could be run into a sheet. In most cases the sugar continued to increase at about the same rate until the 10th hr., after which the reaction slowed down appreciably, although the trend was still sharply upward. The best quality pulp was obtained at the 11th hr., at which time the average quantity of sugar produced corresponded to 11 per cent of the dry weight of the original wood. Those cooks that were carried beyond the 11th hr. produced pulps that were of inferior quality both in color and strength. Apparently considerable hydrolysis of the cellulose occurred after the 12th hr. since a cook of 13¼ hrs. gave the lowest yield of screened pulp of any of this series. During the 12th and 13th hrs. the rate of sugar production was much less, although at no time did the per cent of sugar become constant.

It is of interest to note the rate at which lignin was removed compared with the rate of sugar formation. As will be noticed from Fig. 1, these curves almost parallel each

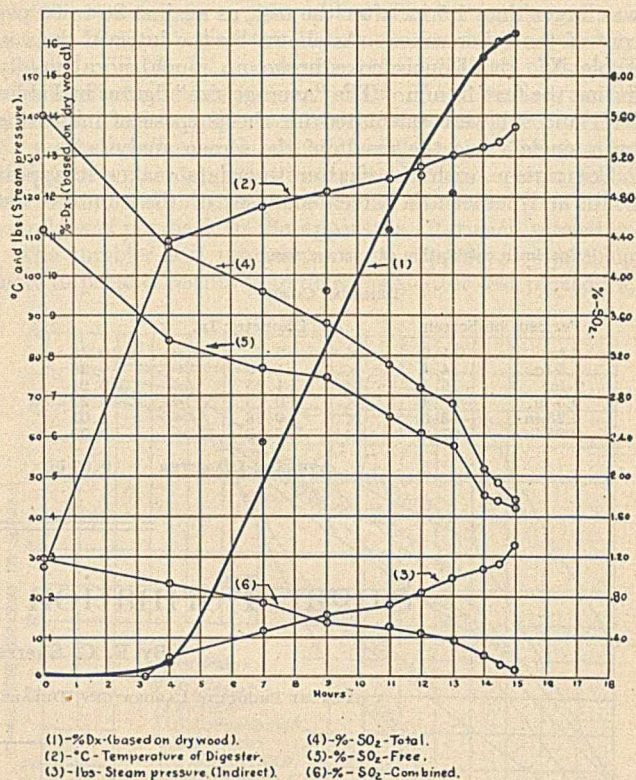


FIG. 3

other until about the 8th hr., at which time the removal of the lignin became much more rapid. When the maximum quantity of lignin (about 90 per cent of the total) had been removed, the quantity of sugar formed corresponded to about 12 per cent of the dry weight of the wood.

Fig. 2 contains typical curves indicating variations in temperature, steam, and gage pressure, sulfur dioxide as total, free and combined, and per cent of sugar (Dx) based on the dry weight of the wood.

The above cooks were carried out using a concentration of sulfur dioxide that averaged 3.80 per cent total, of which 2.39 per cent was free and 1.41 combined. A single cook was also carried out in which the total sulfur dioxide content was 5.60 per cent, composed of 4.46 per cent free and 1.14 per cent combined. The variables in this cook, such as pressure, temperature, etc., are shown in Fig. 3. Here again it was noted that but little sugar was formed before a temperature of 108° C. was reached. With the increased quantity of sulfur dioxide the rate of sugar formation was much more rapid after the 4th hr. than in the previous series and the final yield of total reducing sugar was 16 per cent of the dry weight of the original wood. This increase of about 3 per cent sugar was offset by about a 2 per cent loss in the cellulose yield. The quality of pulp produced in this cook was the best obtained in any of the experiments and compared favorably with the best commercial product. It is our intention to continue the investigation of the effect of increased quantities of sulfur dioxide on the sugar formation in both the Mitscherlich and Ritter-Kellner processes.

An "Association of Manufacturers of Non-Corrosible and Anti-Corrosive Products" is being organized in England by firms making stainless steel, anti-corrosive paints, boiler preservatives, and the like. It is proposed that the association shall act as an institution of anti-corrosion engineers and also as a chamber of commerce for firms making any material or appliance connected with the prevention of corrosion. A public exhibition of noncorrodible and anti-corrosive products is planned for the near future.

The Chemistry of Wood^{1,2}

IV—The Analysis of the Wood of *Eucalyptus globulus* and *Pinus monticola*

By S. A. Mahood and D. E. Cable

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IN THIS article, which is the fourth of a series by the Forest Products Laboratory on the chemistry of wood, the analysis of two new species is reported. The method of analysis employed in the earlier work has been followed closely, except for a modification of the method of preparing a sample for analysis and the inclusion in the analysis of methods for determining lignin and alpha-, beta-, and gamma-cellulose, which progress in the subject seems to justify.

Recent investigations in wood chemistry have been made by Johnson and Hovey³ and Dore⁴ in this country and Schwalbe and Becker⁵ and König and Becker⁶ in Europe. A proximate summative analysis of some California woods has been made by Dore. The values obtained, however, are not strictly comparable with ours, on account of differences in the methods employed.

It is desirable to determine as many well-defined splitting products of wood as possible, but until further progress is made in that direction the summation of the values obtained in an analysis appears to be of secondary importance. To merge the well-defined methoxy and acetyl groups into the ill-defined "proximate constituents," lignin and cellulose, would seem to reverse the order of progress, unless these "proximate constituents" are further analyzed, as in the more recent work of Dore.⁷

SAMPLING

The difficulties encountered in obtaining wood in a form suitable for analysis have been pointed out in a previous paper.⁸ It is believed that the 80- to 100-mesh ground sawdust, the preparation of which is described there, fulfils the requirements: (1) of being a sufficiently representative sample, and (2) of affording material which will be uniformly attacked by reagents and which can be manipulated with facility in the course of the analysis.

TABLE I—EFFECT OF SIZE OF WOOD PARTICLE ON RESULTS OF ANALYSIS
(Values given are in per cent of the oven-dry (105° C.) weight of the wood)

MATERIAL	Determination Number	Ash	Cold Water	Solubility in					Methoxy Groups (CH ₃ O)	Pentosan	Methyl Pentosan
				Hot Water	Sodium Hydroxide 1 Per cent	Ether	Acetic Acid by Hydrolysis				
Ground sawdust passing an 80- but retained on a 100-mesh wire	1	0.26	5.30	8.36	17.91	0.62	1.56		17.80	2.89	
	2	0.27	5.33	8.16	17.90	0.58	1.48	6.87	18.00	2.59	
	Mean	0.27	5.32	8.26	17.90	0.60	1.52	6.87	17.90	2.74	
Sawdust passing a 40-mesh sieve	1	0.21	6.47	9.78	18.09	0.79	1.56	6.64	17.27	3.06	
	2	0.19	6.52	9.69	18.10	0.77	1.34	7.07	17.52	3.00	
	Mean	0.20	6.50	9.74	18.10	0.78	1.45	6.83	17.39	3.03	

To overcome possible objections to Schorger's procedure in using one sample for the cellulose determinations and another sample for obtaining the remaining values in the analysis, material in the same form, namely, 80- to 100-mesh ground sawdust, has been employed for all determinations.

¹ Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922. Published with permission of the Department of Agriculture.

² The earlier papers of this series were published in THIS JOURNAL, 9 (1917), 556, 624, 748, by Dr. A. W. Schorger, whose work the present authors have continued.

³ Paper, 21, No. 23 (1917), 36.

⁴ THIS JOURNAL, 11 (1919), 556; 12 (1920), 264.

⁵ Z. angew. Chem., 32 (1919), 229.

⁶ Ibid., 32 (1919), 155.

⁷ THIS JOURNAL, 12 (1920), 472, 476.

⁸ Ibid., 12 (1920), 873.

For the purpose of determining the variations in results that might be occasioned by this change in the material analyzed, comparable runs were made on samples of *Eucalyptus globulus* in each form. The results, exclusive of the cellulose determinations which are fully considered in the paper already referred to, are given in Table I.

It will be noted that the significant differences between the results in the two series are found in those determinations where surface contact and hence the size of particle comes into play, *i. e.*, the solubility determinations, while the determinations involving partial or complete decomposition of the wood give concordant results. The variations in the values for pentosan and methyl pentosan are probably due to variations in the extraction of the latter.

The somewhat greater solubility in hot and cold water of the material which seemed in the main the coarser of the two led us to sift the 40-mesh sawdust and determine the solubility of the different fractions. The results are given in Table II.

TABLE II—EFFECT OF SIZE ON COLD WATER-SOLUBLE DETERMINATION

Fraction Mesh	Weight of Sample Grams	Soluble in Cold Water Per cent	Weight × Per cent Soluble Content
40-60	16.40	5.47	89.9
60-80	14.60	5.78	84.5
80-100	2.55	5.97	15.2
100-120	3.55	5.83	20.7
120	6.59	8.05	53.1
TOTAL	43.69		263.4

$$\text{Weighted average solubility} = \frac{263.4}{43.69} = 6.03 \text{ per cent}$$

The increase in solubility shown may be due: (1) to decrease in size of particle, or (2) to concentration of the more soluble portions of the wood in the finer material, or both. Since the analytical data, excluding the solubility values, in Table I show the two samples to be uniform in composition,

it is assumed that the increase in solubility shown in Table II is due largely to the effect of the size of particle.

The data show that either form of material will give results that are essentially comparable, but since the 80- to 100-mesh material has been shown to be most suitable for the cellulose determination, this material has been used through the present investigation.

LIGNIN

When the cellulose in wood is removed by hydrolyzing it to soluble forms, a residue is left which is fairly constant, even through the hydrolytic agent and the conditions of hydrolysis are varied somewhat.⁹ The residue retains a surprising similarity to the lignin of the original wood, considering the rather drastic treatment necessary for the

hydrolysis of the cellulose. For example, the residue obtained by treating the wood of *E. globulus* with 72 per cent sulfuric acid gave the characteristic color for lignin when treated with chlorine and sodium sulfite. The changes which occur are apparently superficial and may involve the loss to a greater or less extent of methoxy and acetyl groups and furfural-yielding constituents. The values obtained, however, appear to be sufficiently constant to warrant their determination in an analysis of wood.

Preliminary experiments showed 72 per cent sulfuric acid, employed by Ost and Wilkening⁹ in the hydrolysis of cellulose, to be a more efficient hydrolytic agent and more convenient to handle than hydrochloric acid. There is considerable difficulty in filtering the lignin residues, owing to the more or less colloidal nature of the solution. This can be largely overcome by boiling the solution after dilution.

In order to adopt a method of procedure, it was necessary to determine (1) the time of exposure to the acid necessary to effect complete hydrolysis, and (2) the effect of boiling the solution. By varying the time of exposure to sulfuric acid it was found that a period of 16 to 24 hrs. is sufficient for complete hydrolysis. The values obtained for western white pine, *Pinus monticola*, calculated on the basis of the oven-dry wood, follow:

TABLE III—EFFECT OF TIME OF EXPOSURE ON LIGNIN DETERMINATION

Time of Exposure Hours	Lignin Content Per cent
4	27.77
8	27.32
16	27.09
24	27.03

The effect of boiling is to reduce slightly the yield of non-cellulose material, as shown by the following results, also on western white pine.

TABLE IV—EFFECT OF TIME OF BOILING ON LIGNIN DETERMINATION

Time of Boiling Minutes	Lignin Content Per cent
Not boiled	28.89
15	27.07
45	26.82
120	26.76

It will be noted that a 15-min. boiling reduces the yield approximately 2 per cent, and that practically no further loss takes place on continued boiling.

In view of the above results, the following procedure was adopted for the determination of the lignin values reported in this paper. It is possible that the conditions are not the optimum for hardwoods.

Two grams of air-dried material are extracted for 4 hrs. with a minimum boiling-point mixture of alcohol and benzene. After removal of the solvent by suction the sample is treated with ten times its weight of 72 per cent sulfuric acid. The sample and acid are intimately mixed with a stirring rod, causing the wood to become completely disintegrated after a few hours. After hydrolysis has been allowed to proceed at room temperature for 16 hrs., the acid is diluted to a concentration of 3 per cent. The solution is then boiled under an air-cooled reflux condenser for 2

⁹ C. F. Cross and E. J. Bevan, "Researches on Cellulose," 3 (1905-10), 39.

hrs. The lignin is then filtered on a tared alundum crucible (previously treated with acid), washed free from acid with hot water, dried at 105° C., and weighed.

CELLULOSE

The cellulose values obtained in the analysis of wood are quite constant for conifers on the one hand and broad-leaved trees on the other. The celluloses from these two groups are differentiated by the amounts of pentosan they contain.¹ Future work will probably show other differences, not only between the celluloses from these two groups but also between that from individual species of each group. It seemed desirable, therefore, to introduce into the analysis the mercerization test¹⁰ as a possible means of further differentiating the celluloses isolated by chlorination.

RESULTS

The results of the analysis of four representative samples each of western white pine and eucalyptus are given in Table V. The pine was grown in Bonner County, Idaho, and the eucalyptus in Santa Clara County, California.

DISCUSSION OF RESULTS

In most cases the results parallel rather closely those obtained by Schorger for conifers and broad-leaved trees, respectively. Western white pine is shown to be very similar in composition to longleaf pine, the most notable difference between the two being in their relative solubility in hot and cold water and alkali, longleaf pine being quite appreciably more soluble in all three reagents.

Eucalyptus does not approach the hardwoods already analyzed in this series as closely in composition as western white pine does the conifers. Among the most notable differences is the low-ash content of eucalyptus, which corresponds more nearly with that of the conifers. The yield of acetic acid by hydrolysis from eucalyptus wood is much less than that from the hardwoods previously analyzed. It has been shown, however, that eucalyptus yields nearly as much acetic acid by destructive distillation as the hardwoods ordinarily distilled.¹¹

The cellulose isolated from the two woods contains approximately the same amount of alpha-cellulose. It is interesting to note that the remaining portion of the cellulose in the case of eucalyptus is almost entirely gamma-cellulose, while in the pine it is about equally divided between beta- and gamma-cellulose. These resolution products of the celluloses should be studied further.

The lignin values are higher for pine than for eucalyptus. In other words, the conifer appears to be the more highly lignified, a fact contrary to the usual botanical conception of the relative lignification of these two groups of plants. It should be noted that the cellulose and lignin values for the individual samples compensate, higher lignin values being obtained from samples with a lower cellulose content.

¹⁰ Cross and Bevan, "Researches on Cellulose," 3 (1905-10), 23; Cross and Bevan, "Paper-Making," 1916, 97; Schwalbe, "Chemie der Cellulose," 1911, 637.

¹¹ U. S. Dept. Agr., Bull. 508.

TABLE V—COMPLETE ANALYTICAL RESULTS ON WHITE PINE AND EUCALYPTUS (Results in percentage of oven-dry (105° C.) sample)

SPECIES	Sample No.	Moisture in Air-Dry Sample	SOLUBILITY IN							Methoxy Groups (CH ₃ O)	IN CELLULOSE							
			Ash	Cold Water	Hot Water	Ether	1 Per cent NaOH	Acetic Acid Hydrolysis	Pentosan		Methyl Pentosan	Cellulose	Alpha	Beta	Gamma	Pentosan	Methyl Pentosan	Lignin
Western White Pine (<i>Pinus monticola</i>)	1	6.18	0.21	2.60	3.35	4.42	13.97	1.21	4.38	6.75	3.41	58.53	70.58	18.16	11.26	4.47	1.59	27.22
	2	7.68	0.20	1.73	2.57	4.42	12.70	0.94	4.59	7.19	3.25	62.29	64.34	10.69	24.97	5.66	2.97	24.15
	3	7.00	0.18	3.92	7.25	3.98	15.92	1.37	4.86	6.48	3.33	59.40	74.29	9.17	16.54	5.19	1.68	27.55
	4	7.15	0.19	4.40	4.78	4.63	16.51	1.09	4.41	7.46	2.90	58.61	49.27	27.27	23.46	5.96	1.56	26.82
	Mean	7.00	0.20	3.16	4.49	4.26	14.78	1.03	4.56	6.97	3.22	59.71	64.61	16.32	19.06	5.33	1.95	26.44
Eucalyptus (<i>Eucalyptus globulus</i>)	1	6.99	0.23	2.65	4.41	0.54	16.57	2.31	7.11	21.41	1.97	59.67	67.85	2.11	31.04	20.35	3.92	24.04
	2	6.55	0.20	4.93	6.96	0.52	18.42	1.97	6.37	20.66	2.14	58.53	69.75	0.00	31.25	21.62	2.44	25.24
	3	6.87	0.27	5.31	8.26	0.60	17.90	1.51	6.87	17.90	2.74	56.45	68.99	0.00	31.01	20.10	2.24	25.07
	4	5.90	0.24	5.79	8.27	0.59	21.40	1.62	6.56	20.39	2.48	55.83	21.76	1.26	26.74
	Mean	6.58	0.24	4.67	6.98	0.56	18.57	1.85	6.73	20.09	2.33	57.62	68.86	0.70	31.10	20.96	2.46	25.27

The Calorific Value of American Woods¹

By S. W. Parr and C. N. Davidson

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WOOD as a fuel may have war-time interest only, or it may be a matter of regional concern or of significance in special industries where wood waste accumulates to a point where it must be disposed of. These conditions may in themselves be a sufficient reason for desiring to know the calorific value of such material. There are other reasons also worth mentioning. At the time this work was carried out (1916), at least, there were no values given in the literature for American woods. Similarly, it is not far wrong to state that there were no values that were worth anything given in the literature for any woods in any country. For example, Count Rumford's values are frequently given in works of reference.² His work was done 110 years ago,³ and while he had the correct idea as to the proper method of procedure, his results were little better than approximations. His sample was burned in a current of air and the products of combustion were conducted through a copper coil surrounded by a known volume of water. His thermometer he made himself, but the chief elements of error were doubtless the uncertainty as to the completeness of combustion and the vague ideas concerning the amount or nature of the moisture present in the wood. Again Groves and Thorp, in their work on "Chemical Technology,"⁴ tabulate the heat values for wood as derived by Berthier, Winkler, and Schödler and Peterson. These values refer to partially dry, well-seasoned wood, but the real content of moisture is uncertain. Worse than this, however, is the fact that all these values were determined by calculation from the weight of a lead button reduced from litharge. The equivalent of oxygen taking part in the reaction is used as a measure of the amount of heat, according to the so-called Welter law which held that a fixed ratio existed between oxygen consumed and heat produced, no matter what combinations were involved. The results obtained do not have the value of a good guess and would need to be increased by about 50 per cent to come even approximately near the true values. Berthier's results were published in 1835. This date, together with the method employed, suggests the absurdity of repeating them except as curiosities. They do not have as much merit as Rumford's values obtained some 20 years previous, the errors being about twice as great.

In other works of reference as Poole's "Calorimetry" (1903), Brame's text on "Fuels" (1914), etc., the values quoted are those of Gottlieb.⁵ These values are more recent and have the advantage that they were calculated to the oven-dry basis. He used a calorimeter with oxygen as the medium of combustion, but it was of the constant pressure type, which seems not to have been capable of as great refinement in results as should characterize the values which are to be used continuously as a standard of reference. Results obtained 40 years ago with an apparatus which to-day is not recognized as standard should at least be worked over for correction or verification. In Poole's tables, note should be made of

two results by Mahler, which doubtless are reliable. They are given as "cinder and water deducted," while the seven values of Gottlieb are not indicated in Poole as to their basis of reference. The original article, however, shows that they refer to dry or "moisture-free" material. The moisture factor was determined by drying for 12 to 15 hrs. in a hot air bath maintained at 115°.

It is evident from this brief survey that the determination of the free moisture present is in as much need of review as the calorific value. Indeed, the latter factor is of little worth without the former. Even greater ambiguity is found in the use of terms than is found in the case of coal. Dry wood is understood to mean well-seasoned wood, and there seems to be a reluctance to recognize a sharp line of demarcation between the free moisture and the very large amount of hydrogen and oxygen chemically combined in the H_2O ratio $(C_6H_{10}O_5)_x$ of cellulose.

Our experiments were first directed toward the determination of the "end-point," if there was one, for the free moisture. Was it obscured by uncertain volatilization of sap constituents, or oxidation of unsaturated compounds in the drying process, or possibly an initial breaking down of the cellulose molecule, giving off seemingly free moisture?

Six samples of dry, well-seasoned wood were prepared in the form of fine sawdust. Approximately 1-g. samples were heated at 105° each for 1-, 2-, 3-, 4-, 5-, 6- and 7-hr. periods,

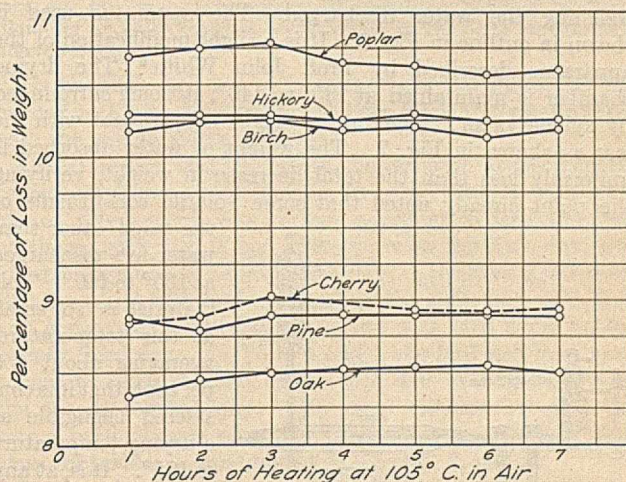


FIG. 1

using a new sample for each period and drying in an atmosphere of air and also in carbon dioxide, using a Freas oven with electric heat control. All samples were cooled 20 min. over concentrated sulfuric acid before weighing. The entire series was repeated at 137°, using an atmosphere of air and repeated with carbon dioxide. The curves show interesting results, but only one of each series is given here. It is evident from Fig. 1 that a substantial equilibrium is established after drying in air at 105° for one hour. A small increase in the air-drying loss is noted up to the end of the third hour. In the use of carbon dioxide as the atmosphere of the oven (not shown) the same percentage of loss is reached at the end of 3 hrs., after which the lines are practically straight.

¹ Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² Groves and Thorp, "Chemical Technology. Vol. 1—Fuel and Its Applications," 1889, 338.

³ Nicholson's Journal, 32 (1812), 105; 35 (1813), 95.

⁴ "Fuel and Its Applications," 1 (1889), 360.

⁵ J. prakt. Chem., 23 (1883), 414.

The conclusion from these curves is that by drying at 105° for one hour in an atmosphere of air, the loss whatever it is, has reached a constant quantity.

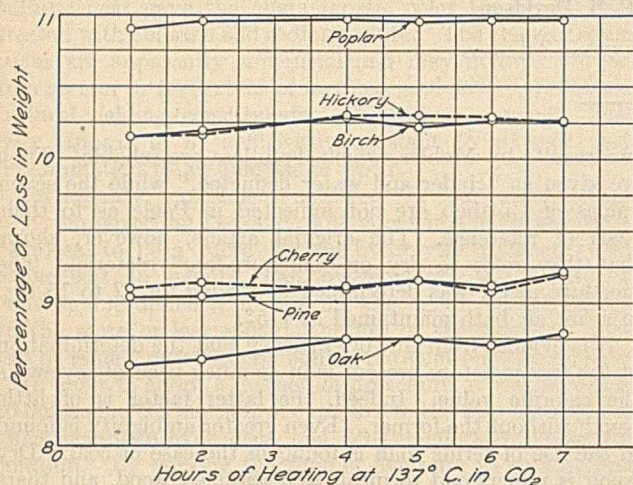


FIG. 2

One other set of curves is worth noting. In Fig. 2 the temperature used was 137° and the atmosphere was carbon dioxide in order to eliminate possible oxidation from the presence of free oxygen. Here the values are stabilized at the end of the first hour, but they are in most cases a trifle higher, usually about 0.2 to 0.3 per cent, though in the case of birch and hickory the difference is not appreciable. The conclusion from a comparison of these two charts suggests the probability of a slight loss of volatile constituents other than water at the higher temperature. This was verified by repeating the drying on a few samples, using the higher temperature with an atmosphere of air and collecting and weighing the water discharged. The apparatus used is shown in outline in Fig. 3. It is a slight modification of the apparatus described by Prof. John White.⁶ The drying chamber is maintained at 135° to 140°, it being surrounded by xylene vapor. The loss in weight is consistent with the loss as shown in Fig. 2. The weight of water absorbed is uniformly less than the total decrease in weight, verifying the point already noted that some volatile constituents of

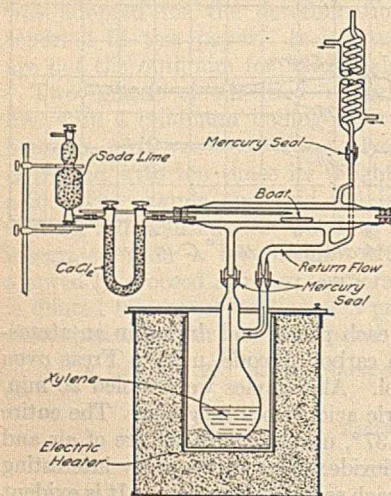


FIG. 3

the wood other than water are discharged at 135° to 140°. This material is so small at this temperature, averaging about 0.3 per cent, that it is considered negligible at a drying temperature of 105°. It is, at any rate, of the same order of difference between water and volatile constituents as the material commonly recognized as being discharged from coal under the same conditions of drying.

In determining the calorific values, the same samples were employed with the moisture content taken as shown after one hour's drying as in Fig. 1, the heat values being calculated to the dry basis. The instrument used was of the Mahler type,

⁶ J. Frank. Inst., 173 (1913), 201.

platinum lined and under adiabatic control by having accessible both hot and cold water for modifying the temperature of the jacketing water to conform to the inner system containing the combustion bomb. The circulation of the jacketing water is secured through the cover as well as on all sides and bottom of the inner receptacle. The results are given in Table I. Corrections were made for the nitric acid formed in the combustion, the fuse wire, etc., as prescribed by the standard method adopted by the AMERICAN CHEMICAL SOCIETY.⁷

TABLE I

Wood	Per cent H ₂ O at 105° C. 1 hr.	B. t. u. (as Recd.)	B. t. u. (Dry Basis)
Pine	8.88	8040.0 8055.5 8054.0	8836.2
	AVERAGE.....	8049.8	
Oak	8.35	7829.0 7855.5 7840.0	8555.7
	AVERAGE.....	7841.5	
Hickory	10.30	7594.2 7561.0 7578.8	8448.1
	AVERAGE.....	7578.0	
Cherry	8.85	7852.0 7867.7 7860.0	8623.0
	AVERAGE.....	7859.9	
Birch	10.18	7607.2 7593.0 7592.2	8458.4
	AVERAGE.....	7597.4	
Poplar	10.69	7709.8 7725.2 7712.5	8639.6
	AVERAGE.....	7716.1	

A comparison with the values as given by Gottlieb for corresponding varieties of wood, so far as they were represented in our samples, will be of interest as follows:

TABLE II—B. T. U. VALUES

WOOD	GOTTLIEB	PARR AND DAVIDSON	DIFFERENCE
Oak	8316	8555.7	+239.7
Pine	9153	8836.0	-317.0
Birch	8586	8458.4	-127.6

An inspection of the table shows that the Gottlieb results have a variation from our own of ± 3 per cent. Considering the fact that woods, even of the same varieties, grown in different countries indicate no greater divergence, it is fair to conclude that the values obtained by Gottlieb should be accepted as reasonably accurate. It must be concluded, however, that considering the care and type of instrument employed in this work, the values as given in Table I fairly represent the correct heat values for the several samples worked on and may be taken as representative values for American woods.

⁷ "Report on Sampling and Analysis of Coal," THIS JOURNAL, 5 (1913), 517.

New Standard Sample of Bureau of Standards

A new standard sample of tin-base bearing metal No. 54 is now being issued with a provisional certificate. This sample has the approximate composition: Tin 88 per cent, antimony 7 per cent, and copper 4 per cent. In addition it contains small amounts of lead, iron, bismuth, and arsenic. The price of this sample is \$2.00 per 140 g., prepaid or parcel post C. O. D.

Benzoic acid No. 48a and benzoic acid No. 39a have been discontinued. Benzoic acid No. 39b replaces both of these and is issued for use both in acidimetric and calorimetric work. The price of this sample is \$2.00 per 30 g.

Studies on Rancidity¹

I—The Influence of Air, Light, and Metals on the Development of Rancidity

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The following paper records experiments on the effect of metals on the development of rancidity in fats and oils.

Fats, even when kept in contact with metals, exposed to light and at summer temperatures, did not become rancid provided that air was excluded. However, the development of rancidity was not prevented when fats, alone and in contact with metals, were kept in a Navy jar through which carbon dioxide, presumably air-free, was passed continuously.

Fats stored, with and without contact with metals, in an atmosphere of oxygen developed rancidity at an earlier date, and the development of rancidity progressed more rapidly, than when the same fats were held in an atmosphere of air, all other conditions being the same.

The development of rancidity was hastened when the fats or oils were in contact with metals, provided there was free access of air or oxygen. Some metals, however, acted more energetically than

others. The action of the metal was independent of the corrosive action of the fat upon the metal. In other words, metals hastened the production of rancidity in fats even when the metals themselves were not attacked.

Light was necessary for the development of rancidity in fats exposed to air and not in contact with metals, but fats stored in contact with metals developed rancidity even when protected from light. In other words, light in the absence of metals appeared to exert the same effect as was exerted by metals in the absence of light.

In one test it was indicated that the direct part taken by moisture in the development of rancidity, at least in comparison with the other factors discussed, is negligible.

It may be concluded that air; oxygen, alone or in combination; light; and metals are among the factors which influence the development of rancidity in fats and oils.

DURING an investigation of the action of fats and oils upon metals² it was noted by one of us that rancidity developed more rapidly when these glycerides were held in metallic containers or in contact with metals than when they were held in glass vessels. Since a search of the literature did not disclose any similar observation by others, the experimental work presented in this paper was conducted.

The detection of rancidity through the sense of smell or of taste, especially in the incipient stage, is not to be relied upon, and therefore in all of the work the Kreis test, which is most sensitive to the chemical changes that finally express themselves in the form of rancidity, was applied at the time the odor was noted. In this test 2 cc. of the fat or oil under examination are dissolved in 2 cc. of a 1 per cent solution of phloroglucinol in ether, 2 cc. of commercial hydrochloric acid are added, and the whole is well shaken, the appearance of any color being noted. Rancid fats cause the development of a more or less pronounced pink shade, the degree of change in the fat being indicated by the depth of color produced. No color is given by freshly prepared fats.

Inasmuch as rancidity was recognized as being due to chemical changes in the fats, the various factors which, during the progress of the investigation, appeared to have an influence either in promoting or retarding its production, were noted, with the view of later determining the part played by each in the phenomena produced.

EFFECT OF METALS AND LIGHT IN PRODUCTION OF RANCIDITY IN FATS EXPOSED TO AIR

SERIES I—The fat used in all of the experiments was rendered in the laboratory from the leaf fat of a freshly killed hog and in each test 60 g. of fat were employed. With but two exceptions (small cups of tin and galvanized iron) the containers were glass vessels of 150-cc. capacity. The metals used were in sheet form, cut approximately of the same size, and rolled into half cylindrical shapes which, when placed on end in the fat or oil, projected slightly above the surface.

¹ Received April 27, 1922. Published with permission of the Department of Agriculture.

² James A. Emery, "The Use of Metallic Containers for Edible Fats and Oils," U. S. Dept. Agr., Bur. Animal Ind., 26th Annual Report, 1909.

Expt. A—Three glass beakers, one containing lard and lead, one lard and copper, and the third lard alone, covered to exclude dust, were placed on a laboratory table exposed to light.

Expt. B—A beaker containing lard and lead, and one containing lard alone, also covered, were placed in a dark closet situated directly under the table mentioned in Expt. A.

Expt. C—Lard in a galvanized iron cup, lard in a tin-plated cup, and lard in a glass beaker, all containers being of the same diameter and also covered, were placed in the light on the table above referred to.

On the fifth day and at frequent intervals thereafter the odor of each sample was noted and the Kreis test was applied, with the results shown in Table I.

It will be seen that the fats in contact with metals became rancid much more rapidly than those in contact with glass alone. The rancid odor became apparent in lard and lead on the seventh day, in lard and copper on the sixth day, and in lard alone on the twenty-sixth day; a positive Kreis reaction appeared with lard and lead on the sixth day, with lard and copper before the fifth day, and with lard alone on the twenty-third day. In Tests 4 and 5 the lard and lead gave a positive Kreis reaction on the fifth day, and lard alone on the twenty-seventh day. The same relation between the rate of production of rancidity in fats kept in metallic and in glass containers, is maintained in Tests 6, 7, and 8.

In regard to the effect of light, there appeared to be no marked difference in the rate of production of rancidity in fats kept in the dark and those kept in the light; however, the evidence upon this point, in view of the limited number of tests, cannot be regarded as conclusive.

EFFECT OF LIGHT ON PRODUCTION OF RANCIDITY

SERIES IV—The results obtained in Series I were considered inconclusive, and since some observers³ have maintained that light is necessary for the production of rancidity, tests were conducted to settle the question more definitely. The samples were placed in blackened light-tight Erlenmeyer flasks, plugged with cotton, and kept under blackened light-tight beakers. The following are the tests conducted:

³ Ritsert, *Naturw. Wochenschr.*, Berlin, 5 (1890), 331, 354, 364; Reinmann, *Centr. Bakt. Parasitenk.*, II Abt., 6 (1900), 131, 166, 209; Scala, *Chem. Zentr.*, 1896, 520; Winckel, *Z. Nahr.-Genussm.*, 9 (1905), 90.

TABLE I—EFFECT OF METALS AND LIGHT IN PRODUCTION OF RANCIDITY IN FATS EXPOSED TO AIR

DATE 1912 4/10	LIGHT				DARKNESS				LIGHT							
	1		2		3		4		5		6		7		8	
	Lard and Lead (Beaker)		Lard and Copper (Beaker)		Lard (Beaker)		Lard and Lead (Beaker)		Lard (Beaker)		Lard in Tin Cup		Lard in Galv. Iron Cup		Lard (Beaker)	
	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test
4/15	—	—	—	+3	—	—	—	+2	—	—	—	+1	—	—	—	—
4/16	—	+2	+1	+4	—	—	+1	+3	—	—	+1	+3	...	+1	—	—
4/17	+1	+3	+2	+4	—	—	+2	+4	—	—	+1	+4	+1	+2	—	—
4/18	+2	+4	+2	+4	—	—	+2	+4	—	—	+2	+4	+1	+3	—	—
4/20	+2	+4	+3	+5	—	—	+2	+5	—	—	+2	+5	+2	+3	—	—
4/23	+3	+5	+3	+5	—	—	+2	+5	—	—	+3	+5	+2	+4	—	—
4/26	+3	+5	+3	+5	—	—	+3	+5	—	—	+3	+5	+3	+4	—	—
5/1	—	—	—	—	+3	+5	—
5/3	—	—	—	—	—
5/7	+2	+1	—	+2	+1
5/24	+4	+2

— = Negative; + = Positive; suffixed numerals used to indicate degree.

This set consisted of two clear 100-cc. flasks, one of which contained 50 cc. of lard, the other 50 cc. of lard in which a sheet of copper had been placed, and of two blackened 100-cc. flasks, one of which contained 50 cc. of lard alone, and the other 50 cc. of lard and a sheet of copper (2 in. by 2 in.).

These flasks were plugged with cotton, and placed upon the table, the blackened flasks being placed under blackened beakers. After 16 days the first observations were made.

	ODOR	KREIS TEST
CLEAR FLASK:		
Lard	Good	Very faint
Lard + Cu	Rancid	Intense
BLACKENED FLASK:		
Lard	Good	Negative
Lard + Cu	Rancid	Intense

As the lard in the blackened flask showed no evidence of rancidity, while the lard in the clear flask showed faint evidences of rancidity, the flasks were kept upon the table for 40 days longer.

	ODOR	KREIS TEST
CLEAR FLASK:		
Lard	Rancid	Intense
Lard + Cu	Very rancid	Very intense
BLACKENED FLASK:		
Lard	O. K.	Negative
Lard + Cu	Very rancid	Intense

The outstanding feature of these tests was that the lard alone in the blackened flask showed no rancidity after 56 days, while the lard in the clear flask was strongly rancid at that time, and probably faintly rancid on the sixteenth day. Further, the lard containing copper in the blackened flask was not quite as rancid after 56 days as was the lard and copper in the clear flask; the difference was so very slight, however, that it may be said that little or no difference exists in the rate of production of rancidity in fats exposed and not exposed to light, when these fats are in contact with metals. A larger number of such tests, with observations made at more frequent intervals, would afford more interesting and more conclusive results than were obtained, and would probably yield valuable information regarding the chemistry of rancidity.

RELATIVE EFFECT OF AIR, CARBON DIOXIDE, AND OXYGEN IN PROMOTING RANCIDITY

SERIES II—Ritsert,³ who studied the effect of air, carbon dioxide, and other gases on fats held in glass containers, found that next to oxygen, carbon dioxide was the most rapidly absorbed. He noted, however, that, although the fats stored in carbon dioxide developed acidity and a flat taste, they did not become rancid.

It is generally believed that the presence of air, or the oxygen of air, is necessary for the production of rancidity. Don-

ath,⁴ whose observations have been confirmed by studies (as yet unpublished) made in this laboratory demonstrated that as a rule fatty acids act upon metals only in the presence of oxygen. The following tests were conducted concerning the rate of production of rancidity in fats stored in atmospheres of air, oxygen, and carbon dioxide:

Fifty grams of freshly rendered leaf lard were placed in each of nine 100-cc. beakers. A sheet of copper was placed in each of three of these, a sheet of tin in each of three others, while to the remaining three no metal was added. The metallic sheets were of uniform size (1.5 in. by 1.5 in.). The beakers were then divided into three groups, each of which consisted of one containing lard and copper, one containing lard and tin, and one containing lard alone. One set was placed on the laboratory table under an open bell jar, another was placed in a Novy jar, through which a stream of oxygen was allowed to flow constantly; and the remaining set was placed in a Novy jar, through which carbon dioxide, obtained by the action of sulfuric acid on marble, was continually being passed. Both the carbon dioxide and oxygen were dried by passing through calcium chloride. Results of these tests are shown in Table II.

In an atmosphere of oxygen, both in the presence of a metal and when no metal was in contact with the fat, rancidity developed at an earlier date, and progressed more rapidly, than in samples held in an atmosphere of carbon dioxide or in air. It was also noted that the fats held in carbon dioxide became rancid a trifle more slowly than did those held in air, although this difference is but slight.

Carbon dioxide had been used in this test solely for the purpose of excluding oxygen. The production of rancidity, and its rather rapid development, in the fats stored in an atmosphere of carbon dioxide was not only not anticipated, but was surprising. While it was believed that the oxygen of the air had been replaced by carbon dioxide, in the Novy jar in which the fats were held, the jar had been opened from time to time for the purpose of extracting samples of fat for examination, and an opportunity was thus afforded for the fat to absorb oxygen. To avoid this the test was repeated in the following manner:

Into each of three 50-cc. beakers, all of the same diameter, 30 cc. of freshly rendered leaf fat which had an acidity of 0.22 per cent (calculated as oleic acid) were added. In one beaker, a square of copper and in a second a square of tin was placed. A third beaker contained the lard alone. The squares of metals each measured 2 in. by 2 in. and were thoroughly cleaned and polished before being placed in the fats.

⁴ Dingers *polytech. J.*, 294 (1894), 186.

TABLE II—RELATIVE EFFECT OF AIR, CARBON DIOXIDE, AND OXYGEN IN PROMOTING RANCIDITY

DATE 1912 6/20	AIR						OXYGEN						CARBON DIOXIDE					
	Lard and Tin		Lard and Copper		Lard		Lard and Tin		Lard and Copper		Lard		Lard and Tin		Lard and Copper		Lard	
	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test
6/28	—	+2	—	+3	—	—	+1	+3	+1	+4	—	—	—	+2	+1	+3	—	—
7/1	+1	+2	+1	+4	—	—	+1	+3	+1	+5	—	—	—	+2	+1	+3	—	—
7/3	+1	+3	+1	+5	—	—	+2	+4	+2	+5	—	+1	—	+2	+2	+4	—	—
7/5	+2	+4	+2	+5	—	+1	+2	+4	+2	+5	—	+1	+1	+3	+2	+4	—	+2
7/10	+2	+5	+2	+5	—	+1	+2	+5	+2	+5	—	+2	+1	+4	+2	+5	—	+2
7/12	+2	+5	+2	+5	—	+1	+2	+5	+2	+5	+1	+2	+2	+4	+2	+5	+1	+3
7/16	+2	+5	+2	+5	—	+2	+2	+5	+2	+5	+1	+3	+2	+5	+2	+5	+1	+3

A second and third set of beakers, identical in all details with the above described, were prepared at the same time.

One set consisting of beakers containing lard, lard with tin, and lard with copper, was placed on the laboratory table, protected from dust but exposed to light and air.

Another set was placed in a Novy jar containing calcium chloride, and through the jar a stream of oxygen, previously dried by passage through calcium chloride, was continuously passed. It was placed on the table beside the first set.

The third set was placed in a second Novy jar, which contained calcium chloride, and through which a stream of carbon dioxide was continuously passed both day and night. The carbon dioxide was generated in a Kipp generator from marble and sulfuric acid, and was washed and dried before entering the jar. The stream of carbon dioxide was interrupted only when it was necessary to recharge the Kipp generator, and on such occasions the jar was closed to prevent access of air. This Novy jar remained unopened from October 14 to November 21. The fats in the first and second sets were tested for rancidity on October 28 and November 8. The results of the Kreis test are shown in Table IIa.

Again those fats held in a Novy jar through which carbon dioxide was passed continuously, developed rancidity. It

TABLE IIa—RELATIVE EFFECT OF AIR, OXYGEN, AND CARBON DIOXIDE IN PROMOTING RANCIDITY

DATE 1912 10/14	Atmosphere of Air			Atmosphere of Oxygen			Atmosphere of CO ₂		
	Lard	Lard and Tin	Lard and Copper	Lard	Lard and Tin	Lard and Copper	Lard	Lard and Tin	Lard and Copper
	<i>Kreis Test</i>								
10/28	—	—	+5	+3	+4	+5	Not tested	Not tested	Not tested
11/8	—	+3	+5	+5	+5	+5	Not tested	Not tested	Not tested
11/21	+2	+4	+5	+5	+5	+5	+1	+4	+5

is true that the complete absence of air, or oxygen, was not proved, but the amount of residual, or adventitious, air or oxygen present must have been, in comparison with the amount of carbon dioxide, extremely small. These experiments certainly indicate that carbon dioxide may promote the production of rancidity. While this observation was considered important and interesting, time did not permit of a more extended investigation.

EFFECT OF EXCLUSION OF AIR ON DEVELOPMENT OF RANCIDITY

SERIES III—Since the rate of development of rancidity in fats stored in air and carbon dioxide appeared to be practically the same, the method which had been planned of securing exclusion of air by replacing it with carbon dioxide, both with and without contact with metals, was abandoned. Complete exclusion of air was obtained by completely filling the container with the melted fat and then forcing a cork stopper into the flask. The fat which was forced out was removed by washing with ether, and the cork was then sealed with wax. The effect of the presence of moisture on the rate of development of rancidity was included in this test. In detail the tests were as follows:

FIRST SET—A 20-cc. bottle was filled with lard, and a second one with lard in which three bright copper strips were placed. The bottles were corked and sealed.

SECOND SET—A 20-cc. bottle was filled with lard, and a second one with lard in which three bright copper strips were placed; 0.2 cc. of water was added to each, and they were sealed and well shaken.

THIRD SET—A 20-cc. bottle was filled with lard and a second one with lard in which three strips of copper were placed; they were allowed to remain open and exposed to the air.

FOURTH SET—A 20-cc. bottle was filled with lard and a second one with lard in which three copper strips were placed; 0.2 cc. of water was added to each, after which they were well shaken, and allowed to remain open and exposed to the air.

The lard used in all of the above tests was freshly rendered from leaf fat and contained 0.22 per cent of free fatty acids calculated as oleic acid. After filling, all bottles were placed upon a laboratory table directly below a window facing the east. They remained upon this table from June 13 to October 1, when they were examined.

FIRST SET—Sealed, no moisture.

Lard alone: Odor, good; Kreis test, extremely faint.

Lard and copper: Odor, good; Kreis test, extremely faint.

No change in acidity was found. Copper had not been attacked.

SECOND SET—Sealed, 1 per cent water.

Lard alone: Odor, good; Kreis test, negative.

Lard and copper: Odor, good; Kreis test, negative.

Copper showed no evidence of having been attacked. The acidity of the lard alone had increased to 0.44 per cent and of the lard with copper to 0.37 per cent, calculated as oleic acid.

THIRD SET—Open in air. No moisture.

Lard alone: Odor, rancid; Kreis test, intense.

Lard and copper: Odor, rancid; Kreis test, intense.

The lard of the lard and copper was green in color, showing that the copper had been attacked.

FOURTH SET—Open in air, 1 per cent water.

Lard alone: Odor, rancid; Kreis test, strong.

Lard and copper: Odor, rancid; Kreis test, intense.

The copper had been attacked, as was evidenced by the green color of the fat.

It is clearly evident from the foregoing tests that oxygen, either free or combined, is an essential in the production of rancidity in fats, whether metals or moisture, or both, be present. Further, direct sunlight and summer temperatures did not cause the production of rancidity in fats which were protected from the access of air. It will also be noted that of the fats in the sealed containers, those in which moisture was present became rancid somewhat more slowly.

PRODUCTION OF RANCIDITY IN CORN OIL AND COTTONSEED OIL AS AFFECTED BY METALS

SERIES V—Corn oil and cottonseed oil do not become rancid as rapidly as animal fats, perhaps on account of the fact that they contain glycerides of the lesser saturated fatty acids. To determine the influence of metals on the production of rancidity in these oils, the following test was conducted:

Cottonseed oil (20-cc. samples) was placed in each of seven 50-cc. glass beakers, and in each of six of these was placed a weighed 0.75-in. square of iron, lead, tin, zinc, copper, and aluminium, respectively. To the remaining beaker no metal was added. They were then allowed to remain for 3 wks. upon a laboratory table exposed to light, when the metals were removed and the loss in weight of each metal, the acidity, and the rancidity of the oil were determined. The results are shown in Table III.

At the same time and under identical conditions, similar tests were conducted with corn oil and lard. In the case of lard, however, changes in acidity were not determined.

The cottonseed oil (iodine value = 105.36; acid value = 0.17) and the corn oil (iodine value = 119.1; acid value = 0.86) were purchased in the open market and represent a good grade of the commercial product.

Rancidity failed to develop in any one of the three samples in which no metal had been placed, although the acidity of both the corn oil and cottonseed oil was slightly diminished. Of the samples of cottonseed oil in contact with metals, those in which iron, lead, and copper had been placed showed, by the Kreis test, marked rancidity, while the one with zinc gave only a slight positive reaction. The samples containing aluminium and tin, when subjected to this test, afforded a blue color, not before noted, but which, nevertheless, was regarded as due to the development of rancidity, or at least to a similar change in the fat. The acidity of all the samples of cotton-

TABLE III—EFFECT OF METALS ON PRODUCTION OF RANCIDITY IN COTTONSEED OIL AND CORN OIL¹

FAT OR OIL	IRON		LEAD		COPPER		ZINC		ALUMINIUM		TIN		OIL OR FAT		
	Original Acidity	Loss Mg.	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Acidity	Kreis Test
Cottonseed	0.17	0.0	0.05	+2	68.3	0.62	+4	1.4	0.11	+1	0.0	0.05	(Blue)	0.0	0.11
Corn	1.86	0.0	1.86	-	44.0	1.69	+1	12.1	1.57	0.0	2.25	0.1	1.35	(Blue)	+3
Lard	..	0.0	..	+4	63.9	..	+5	0.0	..	0.0	+4	0.3	..

¹ Three-week exposure.

TABLE IV—EFFECT OF COATINGS ON METALS IN PRODUCTION OF RANCIDITY

DATE	Lard (Glass Cup)		Lard (Bakelized Tin Cup)		Lard (Tin Cup)		Lard (Bakelized Galv. Iron Cup)		Lard (Galv. Iron Cup)		Lard and Bakelized Copper (Glass Cup)		Lard and Copper (Glass Cup)	
	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test
1912 8/1														
8/6	-	-	-	-	-	-	-	-	-	-	-	+2	-	+2
8/8	-	-	-	-	-	-	-	-	-	-	-	+2	+1	+3
8/10	-	-	-	-	+1	+3	-	-	-	-	-	+3	+1	+3
8/13	-	-	-	-	+2	+3	-	-	-	-	-	+3	+2	+4
8/15	-	-	-	+1	+2	+4	-	-	+1	+2	+3	+4	+3	+4
8/17	-	-	-	+2	+2	+4	-	-	+2	+3	+1	+5	+3	+5
8/20	-	-	-	+3	+2	+4	-	-	+2	+4	+1	+5	+3	+5
8/22	-	-	-	+3	+3	+5	-	-	+3	+5	+2	+5	+3	+5
8/24	-	-	-	+3	+3	+5	-	-	+3	+5	+3	+5
8/27	-	-	+1	+4	+3	+5	-	-	+3	+5	(C)
8/29	-	+1	+2	+5	+3	+5	-	+1	+3	+5
8/31	-	+2	+2	+5	+3	+5	+1	+2	+3	+5

¹ Contained 1.2 mg. copper per 50 g. fat.

seed oil decreased with the exception of that of the oil in contact with lead. Lead in cottonseed oil lost 68.3 mg. in weight, and zinc 1.4 mg.; the other metals suffered no determinable loss. It appears from this that cottonseed oil in contact with metals develops rancidity more rapidly than cottonseed oil stored in glass alone, even when the metals suffer no apparent loss of weight.

Corn oil was not affected as much by contact with metals as was the cottonseed oil; only those samples in contact with lead, copper, and tin developed rancidity. Lead, copper, and zinc lost appreciably in weight; tin, but slightly, while iron and aluminium showed no loss. The original acidity of the corn oil remained unchanged in contact with iron, while in contact with lead, zinc, tin, and copper, and even in glass alone, decreased acidities resulted. The oil in contact with aluminium, however, increased in acidity. It appears that contact with metals promotes development of rancidity in corn oil. Some metals act more energetically than others, but in no case is corn oil as greatly affected as cottonseed oil under similar conditions.

All of the lard samples in contact with metals developed rancidity even when the metal itself was apparently not attacked, while rancidity did not develop in the lard not in contact with a metal.

It will be further noted that the oils in contact with copper developed rancidity more rapidly than those in contact with other metals; those in contact with tin and aluminium were the least affected.

THE VALUE OF PROTECTIVE COATINGS ON METAL IN PREVENTING PRODUCTION OF RANCIDITY

SERIES VI—As metallic containers for fats are by far the most common, having been found by experience to be the most adaptable, and as contact of metals with fats undoubtedly hastens the development of rancidity, an attempt was made to determine the influence of a protective coating of lacquer. The lacquer selected for this purpose was bakelite and was applied in the manner directed by the manufacturer; that is, the thoroughly cleansed metal was painted with the lacquer and, after being dried, was heated while under air pressure.

Copper, tin, and galvanized iron were employed in the test. Portions of lard (100 g.) were placed in a lacquered tin cup, in an untreated tin cup, in a lacquered galvanized iron cup, and in an untreated galvanized iron cup, all cups being of practically the same size. In the test with copper both

lacquered and untreated copper strips of the same size and shape were submerged in separate 50-g. portions of lard contained in 100-cc. glass beakers. With 50 g. of the lard in a glass beaker as a check, all of the samples were placed upon a laboratory table exposed to the light, portions being removed from time to time by carefully melting, stirring, and withdrawing small equivalent amounts of the fat. The results of rancidity tests are shown in Table IV.

It will be noted that in each case rancidity developed earlier in the fat exposed to the unlacquered metal. The difference in the time of appearance of rancidity in the fat exposed with the protected and unprotected copper strips is very slight; however, the lard containing the protected copper strip showed at an early date the green color of copper soaps, and on analysis was found to contain 2.4 mg. of copper per 100 g. of fat, showing that the bakelite coating upon the strips was not intact.⁵

The greatest difference in the time of the appearance of rancidity is found in the case of the galvanized iron cups. In the unprotected galvanized iron cup, the lard was faintly rancid by the Kreis test on the sixth day, while the lard in the protected cup did not give a faintly positive Kreis test until between the twenty-seventh and twenty-ninth days; and, as the lard in glass showed a very faint Kreis reaction on the twenty-ninth day, the protective coating on the galvanized iron cup was evidently efficient.

In the tin cups, the lard in the unprotected cup showed a faint Kreis test on the sixth day, and in the protected cup, between the seventeenth and twentieth days.

These tests indicate:

1—The production of rancidity in fats is hastened by contact with metals.

2—A continuous and unbroken coating of lacquer upon a metallic container effectually prevents the effect of the metal in promoting rapid production of rancidity.

⁵ Copper strips lacquered with bakelite, immersed in lard, were kept exposed to air for several weeks at an elevated temperature of 70° C. with complete protection of the metal.

The American Relief Administration recently forwarded to Russia a consignment of scientific literature selected by various bureaus of the Department of Agriculture, for the purpose of supplying Russian men of science with the results of American scientific work accomplished since 1914. Since that time very few scientific publications from America have entered Russia. Arrangements were made through the American Committee to Aid Russian Scientists with Scientific Literature.

The Determination of the pH Value of Commercial Glucose as a Substitute for the Candy Test¹

By Otto A. Sjostrom²

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In the following paper a simple method is given for the accurate determination of the actual acidity of glucose by means of colorimetric comparison with standards of known pH.

The difficulties and inconveniences connected with the use of the candy test as a measure of the inverting power of commercial glucose are pointed out.

The relation between the inverting effect of glucose as found from the candy test and the pH value for a definite concentration has been determined and expressed in the form of a curve.

COMMERCIAL glucose is used mainly for two purposes; for the mixing and blending of table sirups and for the manufacture of candy. Corresponding to these uses the glucose is manufactured and put on the market in two brands, mixing glucose and confectioners', or crystal, glucose. The mixing glucose is lighter, about 40° Bé., the gravity varying according to the season of the year and to the climate of the territory in which the table sirup is to be consumed. The crystal glucose is furnished in brands of definite gravity, from 42° to 45° Bé. The essential difference between these two brands is that of gravity. In one respect, however, the standards of quality are more definite for the crystal than for the mixing glucose and that is in regard to the acidity of the finished product.

As is well known, dextrose is readily decomposed by the action of even very small amounts of alkali and a slight acidity is therefore essential to the keeping quality of glucose. This acidity is of no detriment in the mixing glucose and might even be considered beneficial, as it promotes the inversion of the cane products with which the glucose is blended. But in the case of crystal glucose an excess of acidity, even if slight, over a certain limit established on the basis of practical experience is detrimental to the quality of the product from the candy-maker's point of view. When in the manufacture of candy glucose is boiled with cane sugar, inversion of the latter takes place to an extent determined by the acidity of the glucose. A small degree of inversion does no harm and is possibly desirable in some cases, but when the formation of invert sugar goes beyond a certain limit the quality of the candy suffers; this applies particularly to the different kinds of so-called "hard candy." The candy becomes hygroscopic or, to speak with the candy-maker, "sticky" very easily. This is due to the presence of levulose, which is more hygroscopic than the other sugars. Of course, under certain conditions of temperature and humidity all candy will become "sticky." There are no particular standards to meet in this respect but the candy-maker knows by experience how much the candy can be expected to stand under certain atmospheric conditions, and when the candy is "out of the ordinary" he lodges a complaint with the glucose manufacturer.

The acidity of glucose is low, usually about 0.01 per cent expressed as HCl, using phenolphthalein as indicator. This acidity is due to acid phosphates and organic acids which are present in varying amounts. It is natural that there should

be certain fluctuations in the acidity of the finished batches of glucose, due to varying conditions in the different stages of a rather complicated manufacturing process and sometimes to differences in the raw material of manufacture. The most convenient way of keeping track of the acidity would of course be to determine the same for each batch by titration, but while this is always done as a matter of record it has long been known that the titration is not a sufficient or correct index of the suitability of glucose for the candy manufacturer. The practice has therefore been to apply a test to the glucose which imitates the conditions under which the product is to be used. This "candy test" is carried out in the following manner:

Glucose, cane sugar, and water in definite proportions are heated in a copper pan at such a rate that the temperature of the mixture reaches 320° F. in 25 min. The contents of the pan are then poured out on a marble slab and left to cool. All operations are carried out according to detailed and rigid instructions. A table showing the relation between temperature and time has to be followed to the second. After cooling, the candy is broken up, an average sample is taken, and from this sample 5 g. are weighed out and dissolved in a 100-cc. flask which is filled to the mark. In this solution the reducing sugar is determined in the ordinary way with Fehling's solution by titration.

The reducing sugar found represents the sum of the dextrose from the glucose used in the test and the invert sugar formed from the cane sugar during the heating. For the sake of simplicity the reducing sugar is all counted as dextrose. The dextrose from the glucose can be calculated from the dry substance of the latter, and a table has been worked out which gives this dextrose as per cent of the total dry substance of the candy for varying purities. In another table the results of the titration for total dextrose are expressed as per cent of total dry substance. The difference between the latter value and the value found from the first table gives the amount of invert sugar in the candy. The permissible maximum of invert sugar has been fixed to 8.5 per cent, and any batch of glucose which gives a higher inversion is diverted to the table sirup department.

The candy test gives also important information about the quality of the glucose in other respects, when interpreted on the basis of practical experience. It is therefore indispensable to the glucose manufacturer.

For general information about the quality of the glucose occasional tests are sufficient. But for information about acidity every batch has to be tested, if the record is to be kept complete, and with only this test available the control work becomes quite a problem for the laboratory, especially if the output of the plant is large.

The test is cumbersome and time-consuming and requires the undivided attention of the operator, who consequently can attend to only one test at the time. The least carelessness on the operator's part results in incorrect data on the acidity effect, as the degree of inversion is very sensitive to any deviation from the time-temperature schedule and the analytical part has to be carried out accurately to give reliable results.

HYDROGEN-ION MEASUREMENTS

It occurred to the writer that sufficient information about the inverting power of glucose could be gained in a much more simple and rapid way by applying some of the prin-

¹ Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² Research Chemist, Corn Products Refining Company.

ciples of physical chemistry to this problem. The varying quantities of organic and inorganic acids in the glucose determine the degree of inversion by virtue of the concentration of the hydrogen ion to which they give rise. The methods for the determination of this concentration have been worked out carefully and are finding widespread industrial application. The investigation was therefore a matter of determining the pH values of a number of glucose samples, the inversion figures of which were known from the candy tests, and expressing the connection between these values in the form of a curve.

Both the colorimetric and the electrometric method have been used. The latter, of course, has its place in an investigation of this nature; but for routine work the colorimetric method is the only one to be considered. It is simple, rapid, quite accurate, if carried out with due attention to details, and—last but not least—almost foolproof.

The pH values of glucose solutions, under the conditions of test which will be spoken of later, range between 3.5 and 5.5 pH. For standard solutions covering this range either the Sorensen citrate mixtures or the more recently suggested phthalate mixtures can be used. The writer from long familiarity prefers the former and cannot find that the latter offer any advantages, in spite of claims for greater convenience in preparation. Besides, citric acid is cheap and can easily be obtained in sufficiently pure quality.

The composition of the citrate mixtures for different pH values is given in Clark's well-known treatise.³ However, the intervals of pH in Clark's table are quite irregular and considerable interpolation is necessary to find the relations for increments of 0.1 pH. The writer has therefore used the excellent diagram found in Michaelis's book,⁴ from which a table can be made up covering the desired range.

The indicator which covers most closely the range in this work is methyl red. For acidities in the vicinity of and above 4.0 pH bromophenol blue would be more convenient, as in this part of the range the color changes of the latter are much more marked than those of methyl red. Besides, bromophenol blue is very permanent, whereas the methyl-red colors fade rather rapidly and can be used only for immediate readings, within half an hour after addition. The great difficulty with bromophenol blue is, however, that the color which it imparts to glucose solutions is of a different quality from that of a standard solution of the same pH. The main difference seems to be that the red is more strongly absorbed in a glucose solution, so that the latter in daylight appears blue, whereas a standard solution is purplish blue or violet. Clark, in the chapter on "Optical Aspects," discusses this phenomenon as observed in turbid solutions with bromophenol blue and suggests the use of a light screen of a certain quality in order approximately to equalize the colors. Accordingly, various screens were tried, but in the case of glucose the difference in color character is so great that it was not possible to devise an arrangement for the equalizing of the colors without at the same time reducing the sensitiveness of the method too far for accurate color comparison. It might be mentioned that by working with electrometric measurements as a guide the eye can be trained to these peculiarities, so that after some practice very close guesses of pH values can be made. Methyl red, however, gives practically the same hue of color with glucose solutions as with the standards and the color changes are sufficiently marked to allow determinations to 0.1 pH, although in the more acid part of the range the changes are of course in the color value rather than in the hue.

For the color comparison a simple comparator on the Wal-

pole principle, such as the one recommended by Clark, answers all purposes. The comparisons are facilitated by the fact that glucose solutions are clear and not at all or very slightly colored. The work should be done in daylight and it is very essential to accuracy that the light be uniform. An excellent illumination for observations is the reflected light from a large plate of white enamel glass, of the kind commonly used for sanitary table tops, which is laid on a table close to a window. In this light all irregularities due to clouds in the sky are eliminated.

In this connection some points concerning the physiological side of color comparison should be mentioned which apply more or less to all colorimetric work. All individual color comparison is eminently a matter of rapid and concentrated action, especially when judging different values of the same color. It is in the first moment of vision that the eye perceives most sharply the difference between values. Prolonged observation only lowers the power of discrimination. The best way to observe is therefore to "flash" the colors. The comparator block is held in a tilted position with the field dark, and by a uniform angular movement of the hand the color disks are made to appear and disappear in the same manner as if a screen were raised and lowered over the observation holes. The operation is repeated as many times as necessary. By working in this way the eye also gets a short rest between each observation, and color values can be read with great accuracy and with very little tiring effect on the eye. Color fatigue from prolonged observation manifests itself in a peculiar way. At first there is a decrease in the power of discrimination; then a rather sudden change takes place into a gross irregularity of perception and the observations become entirely unreliable. Fortunately the eye recovers very quickly from a fatigue of this kind but in the meantime mistakes might easily have been made. It is therefore advisable to guard against errors from this source by making the observations in the manner suggested, by "flashing," especially in the range close to 4.0 pH.

COLORIMETRIC TEST OF GLUCOSE

The colorimetric test of finished glucose batches is made as follows: The samples are first diluted to 22° Bé. This arbitrary concentration has been chosen as a compromise, in consideration of the facts that on one hand the pH value is less influenced by other factors and consequently more representative the less the sample is diluted, and that on the other hand dilution is necessary in order to handle the samples in test tubes and get a uniform mixture with the indicator. A practical point of advantage in regard to dilution is that the gravity does not have to be exactly the same for every sample. The effect on the pH value of a variation of a few tenths on either side of 22° Bé. is so small that it can be neglected.

The comparisons are made on 10-cc. samples of glucose solutions and standards, to each of which exactly 0.2 cc. of a 0.02 per cent alcoholic solution of methyl red has been added. This amount of indicator was determined by experiment. When rather exact information on pH values is needed, as in this case, it is essential to establish as closely as possible that strength of color which will give the maximum of color differences for variations of pH. It was found that with the above amount a maximum of sensitiveness was attained. The strength of color for a given proportion between indicator and volume of solution depends of course upon the lumen of the test tubes used.

By carrying out the color comparisons in the manner described the pH values can be determined to 0.1 pH in the upper, more acid part of the series, and to 0.05 pH in the lower part. For ordinary routine work the standards are made up in increments of 0.2 pH and the pH values estimated to 0.1 pH.

³ "The Determination of the Hydrogen Ions," p. 82.

⁴ Michaelis, "Die Wasserstoff Ionen Concentration," p. 173.

COMPARISON WITH CANDY TEST RESULTS

The numerical relation between the inversion figures from the candy tests and the pH values for glucose diluted to 22° Bé. is shown in Fig. 1. The samples were selected according to candy tests already made and the figure represents the original data upon which the relation was based. From the difference in inversion results for the same pH value it

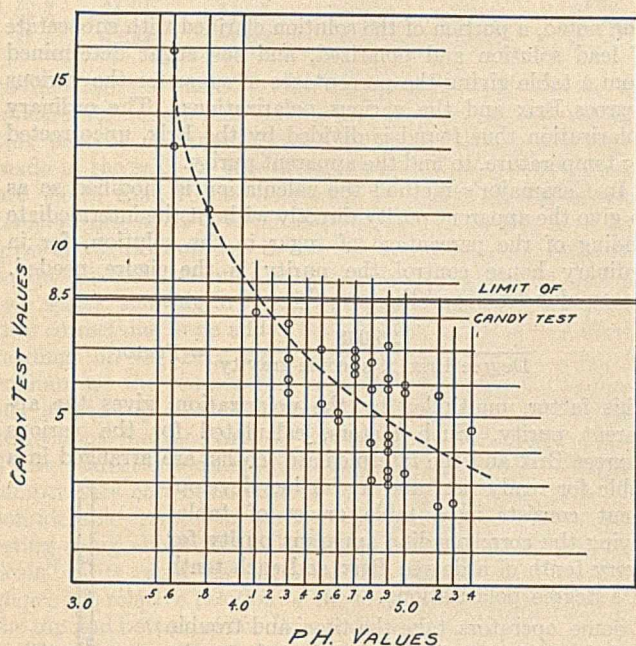


FIG. 1

can be seen that the candy test is far from reliable when made under conditions which require a comparatively large number of tests to be completed within a limited time. It is interesting to note that the points are grouped so as to form a sort of lane and are about equally distributed on both sides of this lane. The curve was therefore drawn through this lane and represents in an approximate way the average of these values. From a great number of additional comparisons in which the candy tests were made with particular care the relation between the values has been found to correspond fairly well to this curve, except in occasionally occurring batches of very high or low pH. Such batches give irregular inversion results. It happens occasionally that the candy test gives an inversion figure quite inconsistent with the pH value, but careful repetition of the test has shown every time that the first result was incorrect and due to an error of some kind in the work.

TABLE I—RELATION BETWEEN pH VALUE AND INVERSION

pH	Invert Sugar Per cent
3.6	16-30 (irregular)
3.7	13
3.8	11
3.9	10
4.0	9.3
4.1	8.7
4.2	8.1
4.3	7.5
4.4	6.9
4.5	6.4
4.6	6.0
4.7	5.6
4.8	5.2
4.9	4.8
5.0	4.5

The average relation between pH value and inversion, as taken from the curve, is shown in Table I.

It has already been mentioned that the limit for invert sugar is set to 8.5 per cent of the total dry substance candy. According to Table I this corresponds to a pH value between

4.1 and 4.2. In order to be on the safe side we have made it a rule to consider 4.3 as the upper limit of acidity. A glucose of 4.3 or higher numerical value is passed without further test. If the value is 4.2, a careful candy test is made and the batch is passed or not, according to the result of this test. The general run of pH values is in the range between 4.5 and 4.9.

The relation which has thus been established between pH value and inversion may not hold in the same numerical way under all conditions, that is, with glucose of less uniform purity than the product manufactured at the plant where this investigation was carried out, or with glucose made under different manufacturing conditions. It is not likely, however, that the difference would be great, and it would at any rate be a comparatively easy matter to find the proper relation with the aid of the information given in this paper.

Note on the Use of the Mohr Pipet¹

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Having frequent occasion to use the Mohr pipet for small titrations, the writer has found the following device of great assistance, and as he has no recollection of having seen this particular application of an old device described in print, it is here given for what it may be worth.

A piece of rubber tubing about 4 cm. in length is slipped over the top of the pipet; a glass bead is placed in the tube, and a short, glass mouth-piece is fitted into the other end of the tube. A slight pressure over the glass bead with the thumb and forefinger allows the pipet to be filled or emptied, and it is readily cleaned after slipping the whole device off the pipet.

This device has the following advantages:

- (1) It prevents the fatigue induced by holding the finger tightly over the top of the pipet.
- (2) It makes no difference whether the fingers be wet or dry, whereas, in the ordinary manner of using the pipet, the finger and the top of the pipet must be reasonably dry.
- (3) It makes possible a greater degree of accuracy in titrations, as the liquid is automatically held in the pipet until released by pressure on the rubber tube, and this pressure can be so regulated as to "split drops" with great ease.
- (4) It is possible to make a series of small titrations with one filling of the pipet, as the pipet can be transferred from one hand to the other, or placed in a clamp-stand while recording results.
- (5) In case the top of the pipet becomes broken or nicked, it is still possible to use it by means of this device.

To obtain satisfactory results, the bead must fit the rubber tube fairly tightly, and it may be found necessary to renew the tube frequently, but the writer has found the device very satisfactory, and well worth the small amount of trouble involved in keeping it in order.

¹ Received June 1, 1922.

Cactus as a Fodder

In those parts of the country where, in the neighborhood of sugar factories, wide areas of land overgrown with cactus are available, the slicing machine and the pulp drier at the sugar works may be used for converting the cactus into a fodder.

The cactus is exposed to a torch to burn the thorns away and then carried to the slicing machine with specially formed knives. These slices are then dried, and if desired they may be ground to a coarse powder. During the slicing part of the juice is pressed out and may be collected separately. It can be converted to a substitute of gum arabic, which is probably a salt of the meta-arabic acid. The yield of dry material is about 11 per cent of the raw cactus.

Sugar Purity Determinations¹

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The following paper describes a method of making sugar purity determinations which can be carried through in not over 60 per cent of the time required for the wet lead method.

The paper describes a special spindle for making Brix determinations in which temperature corrections can be read directly from the instrument. Clarification is accomplished with a specially prepared dry lead powder, eliminating the measurement of exactly 100 cc. and dilution to exactly 110 cc. The paper ends with the description of a table for reading sugar purities, knowing Brix value and polarization. The method eliminates several common sources of error, thus improving quality as well as quantity of the work done in the sugar laboratory.

IN SUGAR manufacture and refining no analytical determination is of such importance as that of the purity. All massecuites are adjusted in purity to the proper degree so that the desired quality of sugar may result, the proper yield be obtained, and the treated material fit in as it should with what precedes and what follows it. Sirups or molasses must be tested for purity to determine that the proper ratio exists between them and the massecuites from which they spring.

A useful factor is the concentration of impurities in sirup as compared with that in the massecuite. Of course, (100—purity) gives the impurities, and it will be immediately apparent that the ratio of the impurities in the massecuite to the impurities in the sirup is a fairly constant factor for similar grades of massecuites. Since these factors progressively lessen as the purity of the massecuite goes down, it will be found a very useful aid in calculating the steps and yields in any proposed procedure in purification by crystallization.

Liquors from boneblack filters must be watched carefully as to purity to allow of proper segregation. So must sweet waters from bags, presses, char filters, or other source, in order to control operations and distribution. Raw sugar affination must also be very closely checked by purity determinations in order to insure sufficient, and to prevent excessive, washing in the centrifugals.

In a large plant, purity determinations form the main guide for chemical control and mount into the hundreds daily. The tests must be made quickly and with such accuracy as is compatible with speed. The procedure must be made as simple as possible.

CALCULATION OF PURITY

The two requisites to calculate the purity of a sample are its percentage of solids and its percentage of sugar. When the solids are determined by evaporation and the sucrose by double polarization, the purity obtained is known as the true purity; when the solids are determined by the gravity of the solution, whether through the pycnometer, the hydrometer, the Westphal balance, or the refractometer, and the sugar by single polarization, the result is called the apparent purity. This is the usual test and there are several ways of performing it. By Schmidt's method, largely used in European beet practice, the density of the solution is determined by a Brix hydrometer, the temperature correc-

tion noted, a portion of the solution clarified with subacetate of lead solution and polarized, and the sugar determined from a table giving the percentages of sugar for the various degrees Brix and the various polarizations. The ordinary polarization thus found is divided by the Brix, uncorrected for temperature, to find the apparent purity.

In Casamajor's method the calculation is modified so as to give the apparent purity directly without the intermediate finding of the percentage of sugar in the solution, for in ordinary house control the purity is the figure needed. Casamajor developed the formula:

$$\frac{26.048}{\text{Degree Brix} \times \text{specific gravity}} = \text{Factor}$$

This factor, multiplied by the polarization, gives the apparent purity. Such factors, calculated for the various degrees Brix and the intermediate tenths, are arranged in a table for ready use, and a further development consists in a table or set of tables giving the corresponding apparent purity for every tenth of a degree Brix and each tenth of a degree polarization.

Some operators take the time and trouble to bring the solution being tested to the normal temperature before determining the degree Brix. If such a solution is also polarized at the same temperature, no error due to effects of changing temperature upon density and specific rotation can creep in. As the errors in polarization are very small for a slight temperature range, they are generally neglected, on account to the great inconvenience and loss of time incurred in bringing solutions exactly to a normal temperature.

The usual manner of determining the apparent purity is to find the degree Brix with a hydrometer in a tall glass cylinder, to observe the temperature of the solution, to clarify the solution with subacetate of lead, filter and polarize, and to calculate the purity from the corrected Brix and the observed polarization.

RAPID DETERMINATION OF PURITY

The following method developed by the writer for obtaining results rapidly and simply may be of use to others.

DENSITY—For rapid Brix determinations a specially constructed spindle, which combines several novel features, has been evolved. The spindle is about 30 cm. over all, with a stem about 15 cm. long. This contains a scale of about 11 cm., covering 8 full degrees divided into tenths, each of which is just about equal to the depth of the meniscus of the solution. The lower part of the spindle is made almost plainly conical to give greater strength in resistance to breakage,



¹ Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.



TABLE OF SUGAR PURITIES

Brix.....	15.1	15.2	15.3	15.4	15.5	15.6	15.7	15.8	15.9	16.0	16.1
(Factor) ..	(1.6221	1.6108	1.5996	1.5887	1.5777	1.5670	1.5564	1.5458	1.5355	1.5253	1.5152)
Pol.											
25.0	40.55	40.27	39.99	39.72	39.44	39.18	38.91	38.65	38.39	38.13	37.88
25.1	40.71	40.43	40.15	39.88	39.60	39.33	39.07	38.80	38.54	38.29	38.03
25.2	40.87	40.59	40.31	40.04	39.76	39.49	39.22	38.95	38.69	38.44	38.18
25.3	41.04	40.75	40.47	40.19	39.92	39.65	39.38	39.11	38.85	38.59	38.33
25.4	41.20	40.91	40.63	40.35	40.07	39.80	39.53	39.26	39.00	38.74	38.49
25.5	41.36	41.08	40.79	40.51	40.23	39.96	39.69	39.42	39.16	38.90	38.64
25.6	41.52	41.24	40.95	40.67	40.39	40.12	39.84	39.57	39.31	39.05	38.79
25.7	41.69	41.40	41.11	40.83	40.55	40.27	40.00	39.73	39.46	39.20	38.94
25.8	41.85	41.56	41.27	40.99	40.70	40.43	40.16	39.88	39.62	39.35	39.09
25.9	42.01	41.72	41.43	41.15	40.86	40.59	40.31	40.04	39.77	39.51	39.24
26.0	42.17	41.88	41.59	41.31	41.02	40.74	40.47	40.19	39.92	39.66	39.40
26.1	42.33	42.04	41.75	41.47	41.18	40.90	40.62	40.35	40.08	39.81	39.55

to increase the area of the thermometer bulb, so as to quicken its action, and to give ease in washing and wiping this part of the instrument. A new departure has been made in the scale of this thermometer. Centigrade degrees are shown from 10° to 35°, with 20° taken as the normal temperature, so as to cover all practical ranges, but these degrees are marked off well to one side. Immediately adjacent to the mercurial column are two direct temperature correction scales, showing in tenths of a degree Brix the temperature corrections to be added to or subtracted from the direct readings on the Brix scale. On one side of the mercury column are the temperature corrections applicable for density at the top of the Brix scale; on the other side are the corrections for readings at the bottom of the Brix scale. These corrections differ quite materially, so that a single temperature correction scale is very deceptive and leads to considerable errors in purity determinations. An interesting thing about this "Complete Temperature Correction Scale" is its rapid visibility, for just as one measures at a glance the relative position of the level of the liquid between the top and bottom of the Brix scale, so he intuitively arrives at the corresponding point between the maximum and minimum temperature corrections, which is to be taken and applied to the particular density reading obtained. In practice the matter is very simple, for usually the Brix is made up arbitrarily to lie quite near one end of the scale. An 8 to 16 Brix spindle is used for the general run of solutions that are rather dark and readings are taken between 15 and 16 Brix, while for lighter colored solutions a 16 to 24 spindle is frequently employed, and solutions are prepared to be read at the end representing the greater density.

Readings are always made to the closest half-tenth, and where unusual accuracy is desired the readings can be made to about a hundredth of a degree by interpolation. Equally close readings can be made on the temperature correction scales.

CLARIFICATION—The density having been obtained, the next operation, that of clarifying the solution for polarization, is greatly expedited by the use of the author's "dry lead" method, in which specially prepared anhydrous lead subacetate is employed in place of basic lead acetate solution. As this dry powder effects the same clarification without producing any alteration in the concentration of the sugar solution, the tedious and frequently inaccurate method previously followed can be greatly simplified. Instead of measuring off 100 cc. of the solution, adding lead solution and making up to 110 cc. with water before filtering, one simply throws out all but about 100 cc. of the sugar solution from the Brixing cylinder, adds with a little scoop a small amount of the "dry lead" powder, sufficient to cause flocculation (each 0.1 cc. of the dry lead is equivalent to 2 cc. of a 28° Brix solution of the subacetate), turns the cylinder over two or three times, and pours all directly upon a filter paper.

Since no correction need be added to the polarization, as was formerly the case to compensate for the dilution of the solution, a source of frequent error is eliminated.

POLARIZATION—For polarizing, a continuous tube is a convenience and saves time, and is good if the solutions

are of nearly the same density, but when the densities of successive solutions change as radically as they do in refinery practice, the intermittent tube is safer. Covering ends that slide on, however, are to be preferred to those which have to be screwed on.

CALCULATION—There remains only the calculation, either by multiplying the polarization by the factor corresponding to the Brix, or by determining the product in some easier way. Various tables and a number of mechanical devices have been constructed for aiding in this operation. The one which the writer has found most convenient for the great majority of solutions tested is a long narrow table of figures giving all the purities corresponding to the different tenths of a degree Brix between 15 and 16 Brix or between any other two consecutive degrees, and the different tenths of a degree by the polariscope. The Brix readings head the vertical columns, while the polariscopic readings stand opposite the horizontal rows of figures. Such a table is about 25 cm. wide and nearly a meter and a half long. This would be quite unwieldy if it had to be used fully extended, and it would be a little inconvenient and subject to excessive wear if it were divided into pages in book form.

A very convenient arrangement which was devised many years ago, however, has proved fully satisfactory. The long paper strip is mounted on two wooden cylinders about 10 cm. in diameter and a little longer than the width of the paper strip. An end of the paper is tacked to each cylinder, and the cylinders are rolled until about half of the strip is wound upon each cylinder and a plane 20- to 22-cm. stretch of paper stands between the two. In this position the whole is mounted in a glass-fronted box and set up in a convenient position for the operator to use. Prior to assembling, each cylinder is bored out longitudinally and a Hartshorn spring shade roller inserted in each, in opposite directions and with ratchets removed. Each spring is given a fairly good tension, so that they tend to pull the two ends of the panoramic roll away from each other, and the whole system remains in practical equilibrium, no matter to which position the paper sheet may be brought. A small windlass handle protrudes from the center of the end of one of the cylinders through the side of the encasing box, so that the operator easily gives it a turn or two so as to expose whatever part of the table he wishes to bring into view.

This device gives great satisfaction to the operators and appears to have suffered no appreciable deterioration after long years of constant use. A part of the table of sugar purities is shown herewith.

According to *Drug and Chemical Markets*, the British dye-stuffs licensing committee proposes to support the domestic dye industry by refusing import licenses when domestic dyes are available in adequate quantities and at reasonable prices. Reasonable prices are considered to be three times the pre-war prices of dyes in general. With regard to vat dyes, reasonable prices for indigo dyes will be two and one-half times and for other vat dyes, five times pre-war prices.

The Precipitate Formed in Sugarhouse Sirups¹

By J. F. Brewster and W. G. Raines, Jr.

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COATES and Slater² in 1916 published a study of the precipitate that forms when clarified cane juice has been evaporated to sirup and allowed to stand. These authors examined two lots of precipitate obtained from two different Louisiana sugarhouses, where plantation white sugar was being manufactured by the sulfitation process. Of the organic constituents of their precipitates Coates and Slater isolated cane wax and found to be present a levorotatory substance which was not sugar. The percentages of ash in their precipitates were 58.0 and 75.6, respectively. The constituents of the ash reported were copper, oxides of iron, aluminium, calcium and magnesium, silica, sulfur trioxide, and phosphorus pentoxide. Coates and Slater conclude that, although the precipitate is made up of substances insoluble in the ordinary sense, it is held in colloidal solution by the heavy sirup, from which it flocculates on standing, particularly when kept hot.

Last year the present writers³ analyzed a sirup precipitate resulting after cane juice had been treated with Filter-Cel and Norit. The ash analysis showed the presence of manganese in addition to the constituents found by Coates and Slater. A thorough study of a similar precipitate has been published very recently by Birckner,⁴ who reported the presence of zinc in addition to the ash constituents enumerated above.

The fact that precipitation invariably occurs in sirup from cane, no matter how brilliant the clarified juice may appear before evaporation, and the fact that it is impossible to obtain high-grade white sugar unless the precipitate is removed, thus forming a distinct step in the process, makes its study important.

The source of the inorganic part of the precipitate-forming substances seems to be an open question. Coates and Slater conclude that the character of the precipitate varied

possible to remove precipitate-forming substances or to reduce the amount of precipitate formed. Cane juice in 10-liter lots was clarified, filtered by means of the laboratory press, and evaporated *in vacuo* to 30° Bé. while warm. The sirup was allowed to stand, and when the precipitate had settled the clear sirup was drawn off by suction and the residue stirred with water and centrifuged. The precipitate was washed three times by centrifuging with water, then thrown upon a filter and washed in the ordinary way until free from soluble matter. It was then dried at 100° and analyzed. As the methods of clarification differed, no refinements in analytical methods were attempted. The dried samples were ashed and after obtaining the weight of ash the latter was fused with sodium carbonate and the methods of silicate analysis applied. No attempt was made to separate the constituents of the ammonia precipitate, which may have contained some phosphates and members of the alkali earth groups. The results for determination of total precipitate and ash are shown in the following table.

The methods of clarification in the first column should be explained. Under the head "sulfur-lime" in Expt. 1, is meant that the raw juice was treated with sulfur dioxide to an acidity of 5.0 cc. and limed back to neutrality against phenol red. The mixture was heated to the boiling point and filtered. The brilliantly clear filtrate was immediately evaporated. In Expt. 2 filter-paper pulp was mixed with the juice, heated, and pumped through the press. The paper proved to be a poor filtering medium when used in this way, the filtrate being cloudy. Norit alone was used in Expt. 3, giving a slightly cloudy filtrate. In Expt. 4, 2 per cent of freshly precipitated and thoroughly washed calcium carbonate was mixed with the juice, heated as in the other experiments, and filtered. The filtrate was brilliant and it

PRECIPITATES FROM SIRUP

Expt. No.	Clarification Method	Ppt. G.	Ash		Analysis of Ash, Per cent					
			G.	Per cent	SiO ₂	Ammonia Ppt.	CaO	MgO	SO ₂	P ₂ O ₅
1	Sulfur-lime	4.1936	3.7121	87.32	23.23	1.11	32.02	None	42.00	0.46
2	Paper	3.4916	2.2161	63.46	9.99	4.13	38.28	None	34.09	0.73
3	Norit	0.5808	26.12	35.97	14.94	1.92	1.67	12.71
4	CaCO ₃	0.0838	53.58	0.24	40.57	None	6.67	3.34
5	Lime Filter-Cel	0.3370	0.1627	48.28	37.95	25.47	26.35	None	1.63	None
6	Lime	0.8243	0.5315	64.48	60.82	8.10
7	Filter-Cel-Norit	1.5118	1.1260	74.47	43.47	2.94	22.72	None	27.48	None

according to the method of clarification. Birckner believes this to be true to a certain extent, particularly in those methods of clarification in which lime is used. The latter author, however, believes that in view of the occurrence of the precipitate in sirups resulting from treatment of juice with kieselguhr and Norit, that is, from treatment without the use of chemicals, it is doubtful whether the precipitate can be attributed, in its main features, to factors not inherent in the cane juice itself.

In making some small-scale clarification experiments, we had as one object to determine whether it would be

was found that the acidity of the juice had been reduced about 50 per cent. Calcium carbonate is an excellent filtering medium and can be used in much less quantity than we employed here. Its use was suggested to us by Dr. Sauer, of the Norit Co., who had tried it previously as a possibility for direct manufacture of white sugar in conjunction with Norit. Expt. 5 was limed to neutrality (phenol red), 0.5 per cent of Filter-Cel added, heated, and filtered. The filtrate was clear. Expt. 6 represents juice limed to neutrality, heated, and filtered. In spite of difficulty in filtering, this mixture was all put through the press, although the filtrate was slightly cloudy. Expt. 7 was a precipitate obtained from the sugarhouse sirup tanks. This juice had been clarified with Filter-Cel, then decolorized with Norit in the presence of a small amount of added phosphoric acid which was neutralized with lime just before filtering. It

¹ Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² THIS JOURNAL, 8 (1916), 789.

³ *Ibid.*, 13 (1921), 923.

⁴ *Louisiana Planter*, 68 (1922), 285.

is to be noted that no phosphoric acid was found in this precipitate.

The cane used in the first six experiments had been windrowed under several inches of earth to preserve it. In Expts. 1, 2, and 3, the cane was unwashed and a considerable amount of adhering soil went into the juice. In Expts. 4, 5, and 6, the mud had been thoroughly removed by washing. Although the figures of the table are incomplete with regard to dry matter of precipitates in 3 and 4, it is easy to draw conclusions from the figures for quantity of ash. The outstanding feature seems to us to be the differences to be noted in total dry matter and ash in the washed and unwashed cane.

Attention should be drawn to the ash content of Expt. 3, where Norit was used on unwashed cane, and the ash content of Expt. 6, where lime only was used upon unwashed cane. Norit was an excellent adsorbent, while the quantity of lime used was too small to be considered of much aid in filtering. The balance is still slightly in favor of the washed cane. The washing of cane before crushing is practiced at many Louisiana sugar factories. One factory, at which this practice had been in force for 4 or 5 yrs., reported in 1919⁶ that the volume of filter-press mud had been reduced 25 per cent. Filter-press mud carries away as much as 6 per cent of sucrose. No mention is made in this report of the influence of cane washing upon the amount of sirup precipitate. The question of sirup settling, however, is discussed and the difficulty of filtering sirup is mentioned. There can be little doubt in view of our results that the presence of adherent soil upon cane would have a great influence upon the quantity of sirup precipitate formed. This is not surprising when it is considered that soil may contain much matter, both organic and inorganic, in the colloidal state which could readily escape removal by our present clarification methods, including those in which highly adsorbent carbons are employed. It is evident that the formation of precipitate may be attributed to three possible sources—namely, from materials used in clarification, particularly in clarification by means of chemicals as suggested in the article of Coates and Slater, from substances present in cane juice itself, as suggested by Birkner and as substantiated by our results with washed cane, and finally from soil adhering to the cane at the time of crushing.

The amount of precipitate that one may obtain from sirup cannot be predicted from the appearance of the filtered juice or sirup. The filtrates and sirups in Expts. 1, 4, and 5 were clear. Those in Expt. 2 were very turbid, while in Expts. 3 and 6 the liquids were slightly cloudy. In some cases the precipitate had a tendency to fall readily after evaporation and in others there was no precipitation until the sirup had been heated to nearly 100° C.

As pointed out by Coates and Slater, filtration of the sirup for the removal of turbidity or precipitate would be too costly and troublesome, and settling appears to be the most feasible method of handling such sirup. It should be added that even when decolorization with carbon is performed at the sirup stage, a precipitate is to be found in the decolorized product. The precipitate analyzed by us last year resulted from such treatment. There is the possibility, of course, that to some extent precipitate-forming substances may be derived in the colloidal state from the so-called inert filtering media. With settling as the most feasible means of dealing with sirup precipitate, it becomes obvious that two conditions are to be sought. These are rapidity of settling and compactness of sediment. This suggests that the addition to the sirup, after it has been run to the settling tanks, of some adsorbent heavy enough to quickly subside and carry

suspended matter with it, might answer the purpose. Fuller's earth, precipitated chalk, and calcium phosphate are substances we have tried and which show promise in this connection.

A Prescription for Hale, Hearty Life

By H. W. Jordan

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Each October we are confronted by the choice of wasting the year's two hundred long, cool evenings in aimless, casual entertainment, or of devoting them to wholesome recreation, balanced by sound reading and study. Repeatedly we see men past fifty, retired from active business by choice or circumstance, who mysteriously fade and soon die. Investigation usually discloses the fact that the victim had no impelling mental interest outside of business routine. Like all complex apparatus shut down or thrown on the scrap heap, he quickly disintegrated. Psychologists have proved that we must grow or go. Post-mortem examination of our friend's mind reveals the reason of his going. He had ceased to grow. He knew only one subject, his daily vocation.

Among ways of attaining active age none is better than to hold oneself rigidly to an annual program of reading, designed to impel creative thought. Not the habit of nightly wading through thirty-two pages of the metropolitan daily, an action interspersed with naps and subconsciousness, barely aware that we are momentarily hibernating until aroused by a tearful voice, "Mercy, it's twelve o'clock. Aren't you ever coming up, dearie?" Instead, a program of three to ten hours weekly devoted to earnest study of a group of subjects wholly outside personal business—history, travel, science, art, or music—to educate, to draw us out of and beyond our technical horizon.

If one seeks examples of such use of spare time he only need scan the biography and books of Theodore Roosevelt or Lord James Bryce to learn the unbelievable extent to which busy, practical men can carry systematic reading, and the value of the knowledge they thus acquire.

This century is destined to be characterized by enormously increased, practical understanding of the human mind, just as the nineteenth century was by colossal applied knowledge of material forces. Exceptional profit and marked individual success is to be won in commerce and engineering industry by correct application of laws which govern the human mind, as inexorably as gravitation and atomic weight rule material action. The Rockefellers and Carnegies of 1950-75 will be industrial executives who have correctly applied this new knowledge of man's mind to the greatest good of the greatest number.

A new, extensive literature has sprung up as a result of the war. It is devoted to the psychology of industrial social life, to a new interpretation of the Golden Rule which is the law of equal action and reaction, to the biology and evolution of states and nations, to mathematical analysis of conservative investment, and to the ebb and flow of mass mind in the seething action of industry and government. Among its authors are Edwin Grant Conklin, Madison Grant, Lothrop Stoddard, Walter Lippmann, Raymond Pearl, James Harvey Robinson, Arthur Pound, Norman Angell, Glenn Frank, Roger W. Babson, Dr. Coué, the French medical psychologist, Anatole France, Walther Rathenau, Guglielmo Ferrero, and John M. Keynes. Their books and their articles in our current magazines need be incorporated in our chemical and engineering subconsciousness. If you would be hale and hearty, devote the winter evenings of 1922-23 to the works of these writers.

⁶ Louisiana Planter, 62 (1919), 187.

Ethyl Alcohol from Western Larch—*Larix occidentalis*, Nuttall¹

By E. C. Sherrard

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A method is given for the fermentation of 70 to 80 per cent of the total sugar resulting from the acid hydrolysis of western larch. This method is equally satisfactory for the fermentation of galactose alone.

Alcohol yields are given both for the water extract and for the solution obtained by the hydrolysis of the wood.

IN 1916 Schorger² called attention to the presence of a water-soluble substance, galactan, in western larch. This material constitutes from 8 to 17 per cent of the wood and upon treatment with dilute acid hydrolyzes to give galactose. Schorger established its identity by several means but was unable to obtain a satisfactory fermentation; the best results obtained indicated a yield of about 40 per cent of alcohol when "S. Carlsbad I" yeast was used.

Because of the large quantity of hexose sugar preëxistent in the wood, Kressman³ concluded that western larch would be one of the most valuable raw materials for the production of ethyl alcohol. He hydrolyzed the wood and obtained yields of total reducing sugar that corresponded to 26.21 to 30.52 per cent of the original material. His fermentation experiments showed, however, that, while the sugars resulting from the hydrolysis of the cellulose were removed, the galactose remained practically unchanged.

A means of completely fermenting galactose is highly desirable, not only because of the high content of hexose sugar in western larch, but also because of the large quan-

in addition to that contained in the galactan this wood should be an excellent source of ethyl alcohol.

EXPERIMENTAL

In order to study the fermentation of these sugars more readily the work was divided into three parts. In the first case the galactan was extracted from the wood with hot water, and then hydrolyzed by boiling for 4 hrs. after the addition of a sufficient quantity of sulfuric acid to make a 4 per cent solution. The galactose solution was then neutralized with calcium hydroxide and evaporated under reduced pressure until a solution was obtained that contained about 5 per cent total reducing sugar. This solution was then fermented as described below.

In the second experiment the residue remaining after the water extraction was hydrolyzed in the usual way, *i. e.*, it was digested in an autoclave for 15 min. at 115 lbs.' steam pressure with a quantity of sulfuric acid corresponding to 1.8 to 2.5 per cent of the dry weight of the wood. The wood was moistened with one and a quarter parts of water in order to insure a complete reaction. The resulting sugars were then extracted with water, the sulfuric acid neutralized with calcium hydroxide, and evaporated as before after the removal of the calcium sulfate by filtration.

In the third experiment the unleached larch was hydrolyzed under the same conditions as stated above, and the sugars extracted and prepared for fermentation in the same way

SUGAR AND ALCOHOL YIELDS

EXPT.	TREATMENT	Total Reducing Sugar Per cent	Total Sugar Fermentable Per cent	Theoretical Alcohol Per cent of Dry Wood	Actual Alcohol Per cent	Fermentation Efficiency Per cent	Alcohol Calcd. 95 Per cent per Ton of Dry Wood	Hydrolysis		
								Sulfuric Acid Per cent	Time	Pressure
I	Water-soluble portion	10.11	79	4.08	4.10	100.5	12.7	4	4	Atmos.
	Autoclaved residue	19.64	69	5.66	6.15	108.7	19.0	1.8	15	115 lbs.
	TOTAL	29.75		9.74	10.25		31.7			
II	Water-soluble portion A	12.37	75.4	4.76	4.69	98.5	14.75	4	4	Atmos.
	Water-soluble portion B	12.37	76.66	4.84	4.84	100.0	15.0	4	4	Atmos.
	Water-soluble portion C	12.37	80.50	5.09	5.09	100.0	15.8	4	4	Atmos.
	Water-soluble portion D	12.37	78.53	4.96	5.40	109.0	16.7	4	4	Atmos.
	AVERAGE	12.37	77.77	4.91	5.00	101.9	15.56			
	Autoclaved residue A	18.00	70.51	6.58	6.80	105.0	21.0	1.8	15	115 lbs.
	Autoclaved residue B	23.07	70.02	8.25	8.99	109.0	26.2	2.5	15	115 lbs.
	AVERAGE	20.53	70.26	7.36	7.89	107.0	23.6			
III	Original wood autoclaved A	28.66	73.6	10.78	10.51	97.5	32.6	1.8	15	107 lbs.
	Original wood autoclaved B	29.35	72.0	10.78	10.78	100.0	33.4	2.5	15	107 lbs.
	AVERAGE	29.00	72.8	10.78	10.65	98.7	33.0			

ties of available waste. In addition to mill waste, such as sawdust, shredded slabs and edgings, a certain logging waste is encountered in the woods, owing to the fact that the butt logs produce an inferior grade of lumber and are so heavy that they prevent rafting. As a consequence, many of these logs of high galactan content are left in the woods. Since the butt logs contain the greatest amount of galactan (10 to 25 per cent) found in the tree, they constitute one of the best sources of this material. Other species of coniferous woods yield an average of 22 per cent total reducing sugar upon hydrolysis with dilute acid, so it is evident that if a similar quantity of sugar is obtainable from larch cellulose

as before. The sugar yields and fermentation data are set forth in the accompanying table.

Experiment I was a preliminary run to determine the most suitable conditions for carrying out the reaction. The sugar yields in all experiments are given as total reducing sugar in terms of glucose and were obtained by means of Fehling's solution with subsequent electrolytic deposition of the copper oxide. In Expt. II four check fermentations (A, B, C, and D) were carried out on the galactose solution. The yeast used in II-D had previously been used to ferment II-C which had, in turn, been obtained from the fermentation of II-B. With these exceptions, the experiments listed in the table were carried out with fresh yeast that had been propagated on malt wort.

The yeast used for the actual fermentation was a pure strain culture of a Hungarian beer yeast, *Saccharomyces*

¹ Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922. Published with permission of the Department of Agriculture.

² THIS JOURNAL, 8 (1916), 494.

³ U. S. Dept. Agr., Bull. 983.

cerevisiae, which has been in use at the Forest Products Laboratory for several years and has proved very efficient in the fermentation of sugars resulting from the hydrolysis of wood.

The sugar solutions were prepared for fermentation by evaporating to a suitable concentration and then adding a sufficient quantity of 10 per cent solution of *autolyzed* yeast to make the whole correspond to a 2 per cent yeast solution. The yeast water was prepared according to the method of Fred and Peterson by boiling autolyzed yeast with distilled water for one hour and filtering while hot. The solution was then again boiled, filtered, and finally sterilized in an Arnold steam sterilizer.

DISCUSSION OF RESULTS

In the fermentation of the sugars resulting from the autoclave cooks of the extracted residue no precautions are necessary other than those already described.³ In order to obtain a satisfactory fermentation of the solutions containing galactose, however, it is imperative that the temperature and acidity be carefully regulated. The temperature must be held between 85° and 90° F., and the initial acidity of the solution not greater than 5°. If the acidity is greater little or no fermentation takes place. When the galactose solution is fermented alone, but very little increase in acidity occurs as the fermentation progresses, but when the solution re-

sulting from the hydrolyzed wood is fermented, an increase of 4° acidity is quite common.

In view of the difficulty formerly encountered in the fermentation of galactose, it is quite surprising that such good results are obtainable under the conditions outlined in this paper. In all cases the fermentation took place better in the galactose solution than in the liquor containing the mixed sugars. In Expt. II the minimum total yield was 35.95 gal. of 95 per cent ethyl alcohol per ton of dry wood, while the maximum was 42.9 gal. The average yield from this was 39.9 gal., by far the largest yield of alcohol obtained from any wood. In Expt. III, in which the mixture sugars were used, the average yield was 33 gal. of 95 per cent ethyl alcohol per ton of dry wood. This lower yield is no doubt due to the greater acid-forming tendency of the sugars other than galactose, with a consequent inhibition of the yeast in the fermentation of the latter sugar. Even in this case the yield was almost 10 gal. greater than from any of the woods previously studied.

The fact that galactose from western larch can be fermented readily with the production of ethyl alcohol is particularly interesting from the standpoint of the paper-maker, since by an extraction of his chips with water before pulping a quantity of sugar is obtainable that is easily convertible into ethyl alcohol.

Radioactivity of Miscellaneous Waters Examined in the Bureau of Chemistry^{1,2}

By W. W. Skinner and J. W. Sale

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From the experience of the Bureau of Chemistry, in analyzing commercial bottled waters of natural origin, and from published data, it may be concluded that shippers of these products are not justified in making any statements on the labels which will induce prospective consumers to purchase the articles because of their radioactivity.

THE ENFORCEMENT of the Federal Food and Drugs Act of 1906 necessitates the examination of mineral waters and other products for content of radioactivity. Consequently the Water and Beverage Laboratory was equipped with three electroscopes of the emanation type, an alpha-ray electroscope, the apparatus designed by Boltwood³ for separating and collecting emanation, and other apparatus necessary for making analyses of the radioactivity of various products. This equipment, the methods used in calibrating the electroscopes, determining the radioactivity of samples, and reporting results have been described in a previous communication⁴ from this laboratory.

Foreign and domestic bottled mineral waters, pads, ointments, capsules, sediments, and other products classified as drugs, coming within the jurisdiction of the Act, are examined, if their labels bear statements relating to radioactivity. In addition to official samples of this nature, the laboratory

has examined a few spring, river, lake, and ocean waters collected by Bureau representatives for the purpose of obtaining data for use in litigation.

In the examination of bottled waters, it is usually sufficient to determine the activity as received, in which case before removing the stopper the sample is chilled, opened, the contents acidified, and poured carefully into the boiling-out flask. Agitation of the water is avoided after the sample is received in the laboratory. Ordinarily, no attempt is made to determine the activity of the gas in the neck of the bottle, since only the emanation or radium salt, dissolved or suspended in the water, is consumed. As we have usually no knowledge of the exact time when the water is bottled, it is obviously impracticable to calculate the initial activity of the water at source by using the accepted formula which represents the rate of decay of emanation. We do make this calculation, however, on samples collected from source for investigation purposes when adequate precautions are taken. It is desirable sometimes to determine whether or not activity is due to the presence of radium salts dissolved or suspended in the water, in which case the permanent activity is determined in the ordinary manner.

In the accompanying table, the results have been expressed in grams of radium $\times 10^{-9}$ per liter, corresponding to activity found. This unit is known also as millimicrogram, and is one billionth of a gram. The letter I in the column of results means that the time of collection of the sample was known and the initial activity, I, of the sample has been calculated; R indicates that the value in the table represents the activity of the sample as received in the laboratory, which may or

¹ Presented before the Division of Water, Sewage, and Sanitation at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

² Published with permission of the Department of Agriculture.

³ *Phil. Mag.*, [6] 9 (1905), 599; *Am. J. Sci.*, [4] 18 (1904), 378.

⁴ "Determination of Radioactivity," *J. Assoc. Official Agr. Chem.*, 2 (1916-17), 116.

RADIOACTIVITY OF MISCELLANEOUS WATERS

No.	TYPE	LOCATION	DATE OF EXAMINATION	Quantity of Water Used Liters	Grams Radium $\times 10^{-9}$ per Liter Corresponding to Activity Found
<i>Waters collected at source by a Bureau representative¹</i>					
1	Cold spring	Virginia	Nov. & Dec. 1911	2.0 (approx. ²)	0.023 R; 0.05 I
2	Cold spring				0.062 R; 0.21 I
3	Cold spring				0.171 R; 0.21 I
4	Cold spring				0.062 R; 0.09 I
5	Cold spring				0.052 R; 0.06 I
6	Hot spring				0.232 R; 0.33 I
7	Hot spring				0.754 R; 1.10 I
8	Hot spring				0.167 R; 0.28 I
9	Cold spring				0.005 R; 0.007 I
10	Cold spring				0.043 R; 0.06 I
11	Cold spring				0.758 R; 0.93 I
<i>Miscellaneous waters collected at source by a Bureau representative²</i>					
12	Philadelphia tap water	Pennsylvania	June 1917	2.3	None or not more than 0.002 R
13	Washington tap water	Potomac R., D. C.	June 1917	2.3	Not more than 0.002 R
14	Reading tap water	Maiden Cr., Pa.	May 1917	2.3	0.006 R; 0.002 P
15	Lancaster tap water	Pennsylvania	May 1917	2.3	None or not more than 0.002 R
16	Mississippi River	St. Louis, Mo., unfiltered	May 1917	2.3	None or not more than 0.002 R
17	Lake Michigan	Chicago, Ill.	May 1917	2.3	None or not more than 0.002 R
18	Atlantic Ocean	4 mi. off Atlantic City, N. J.	June 1917	2.3	None or not more than 0.002 R
19	Lake Erie	4 mi. from Buffalo, N. Y.	June 1917	2.3	None or not more than 0.002 R
<i>Domestic bottled waters</i>					
20	Cold spring ¹	Wisconsin	Sept. 1912	2.4	0.037 R; 0.063 I
21	Cold spring ¹	Wisconsin	Sept. 1912	2.4	0.038 R; 0.076 I
22	Warm spring ¹	Massachusetts	July 1914	2.4	0.188 R; 0.070 I; 0.002 P
23	Cold spring ¹	Massachusetts	July 1914	2.4	0.042 R; 0.183 I; 0.002 P
24	Warm spring ²	Massachusetts	June 1915	2.4	None or not more than 0.002 P
25	Warm spring ²	Arkansas	June 1916	1.0	None or not more than 0.005 R
26	Deep well ²	Ohio	June 1916	0.1	None or not more than 0.050 R
27	Cold spring ²	Arkansas	May 1917	2.3	None or not more than 0.016 P
28	Cold spring ²	Arkansas	May 1917	2.3	None or not more than 0.004 P
29	Cold spring ²	Arkansas	Oct. 1917	2.2	None or not more than 0.002 R
30	Cold spring ²	Wisconsin	Nov. 1917	1.0	None or not more than 0.005 R
31	Cold spring ³	Mississippi	Jan. 1918	1.0	None or not more than 0.009 R
32	Cold spring ³	Arkansas	May 1920	1.0	None or not more than 0.005 R
33	Cold spring ^{3,4}	Mississippi	Oct. 1920	1.0	None or not more than 0.005 R
34	Deep well ^{3,4}	(Dup. of No. 26) Ohio	Nov. 1920	1.0	None or not more than 0.270 P
<i>Imported bottled waters</i>					
35	Cold spring ²	France	May 1914	1.0	None or not more than 0.005 R
36	Cold spring ²	Spain	July 1914	2.4	0.079 R (0.031 P)
37	Cold spring ²	Spain	Jan. 1915	1.0	None or not more than 0.005 P
38	Cold spring ²	Japan	Jan. 1915	1.0	None or not more than 0.005 P
39	Cold spring ²	Italy	Feb. 1915	1.0	None or not more than 0.005 P
40	Cold spring ²	Norway	June 1917	0.5	None or not more than 0.010 R
41	Cold spring ²	Spain	Aug. 1917	0.25	None or not more than 0.020 P
42	Cold spring ²	France	Aug. 1917	0.25	None or not more than 0.020 P
43	Cold spring ²	Spain	Feb. 1918	0.25	None or not more than 0.020 P
44	Cold spring ⁴	Austria	Jan. 1921	1.0	None or not more than 0.005 R
45	Cold spring ⁴	Italy	Jan. 1921	1.0	None or not more than 0.005 R
46	Cold spring ⁴	Portugal	Apr. 1921	0.19	None or not more than 0.11 R

¹ Analyst W. D. Collins.² Analyst F. B. Furber.³ Analyst J. W. Sale.⁴ Analyst W. E. Shaefer.⁵ Either 2.0 or 2.4 liters taken.

may not be due to radium salt contained in the sample. P indicates permanent activity, due wholly to radium salt contained in the sample.

The electroscopes have a limit of sensibility corresponding to 0.005×10^{-9} g. of radium. It is desirable to boil out emanation from about 2 l. of water, in which case as little as 0.002×10^{-9} g. of radium per liter can be measured. Sometimes, however, especially in the case of foreign waters, we have available for this determination only about 200 cc., in which event the least quantity that can be measured is 0.025×10^{-9} g. radium per liter.

The significance of the data depends on the fact that we have never found in any commercial bottled water of natural origin sufficient radioactivity, either temporary or permanent, to warrant its purchase by consumers because of its content of radioactivity.

The largest quantity of radioactivity of a temporary nature which we have found in any commercial foreign or domestic bottled water of natural origin corresponds to 0.188×10^{-9} g. radium per liter. This sample came from a warm spring in Massachusetts.

The largest quantity of radioactivity of a permanent nature which we have found in any commercial foreign or domestic bottled water of natural origin corresponds to 0.270×10^{-9} g. (millimicrogram) radium per liter (Sample 34 in table). The activity of this sample as received was not determined. This sample came from a deep well in northern Ohio.

Let us consider the significance of the two maximum figures just mentioned, 0.188 and 0.270, from a therapeutic standpoint. In "New and Nonofficial Remedies" of 1921, page 254, it is stated that the Council on Pharmacy and Chemistry of the American Medical Association will not accept any

radium solution for internal use, the dosage of which is less than 2 micrograms each day, or any radium emanation generator which yields less than 2 microcuries of emanation during each 24 hrs. It is obvious, therefore, that to obtain the minimum daily dose of emanation from Sample 22 it would be necessary to consume 2810 gal. of water daily ($\frac{2000}{0.188 \times 3.785} = 2810.6$), and to obtain the minimum daily dose of radium salt from Sample 34 it would be necessary to consume 1957 gal. of water daily ($\frac{2000}{0.270 \times 3.785} = 1957.0$). It may be mentioned in this connection that Sample 34 is very highly mineralized, and the dose is measured by the teaspoonful.

Mellon Institute Bibliographic Series, Bulletin 1

The Mellon Institute of Industrial Research has commemorated the tenth anniversary of the use of the Industrial Fellowship System of the University of Pittsburgh by issuing Bulletin 1 entitled "A List of the Books, Bulletins, Journal Contributions, and Patents by Members of Mellon Institute of Industrial Research, 1911-1922." This is the first bulletin of the kind issued by the Institute and is the beginning of a bibliographic series which it is planned to publish. One of the provisions under which the Institute was founded is the dissemination of information concerning investigations carried out under its auspices, and this bulletin represents the published contributions of the Institute to scientific and technical literature from the inauguration of the system on March 1, 1911, to January 1, 1922. The compilation was made by Mrs. Clara Guppy Statler, and the style is that usually followed in bibliography. In listing periodicals the abbreviations of the AMERICAN CHEMICAL SOCIETY have been followed throughout.

Studies in Rubber Vulcanization¹

The Relation between Chemical and Physical State of Cure of Rubber Vulcanized in the Presence of Certain Organic Accelerators

By Norman A. Shepard and Stanley Krall

RESEARCH LABORATORIES, FIRESTONE TIRE & RUBBER CO., AKRON, OHIO

Hexamethylenetetramine, p-nitrosodimethylaniline, aldehyde ammonia, and the thiocarbanilide, respectively, have been introduced in such quantities in a mixing consisting of 48 parts of first latex crepe, 48 parts of zinc oxide, and 3 parts of sulfur, that equivalent physical states of cure (as gaged by the stress-strain relations) have been obtained when vulcanized for 60 min. at 287° F. (141.7° C.).

The amounts of these accelerators required to give equivalent physical states of cure were 0.5 part hexamethylenetetramine, 0.25 part of paranitrosodimethylaniline, 0.75 part aldehyde ammonia, and 1.5 parts of thiocarbanilide, respectively.

The vulcanization coefficients on these matched 60-min. cures, which were 0.87, 1.03, 0.98, and 1.38, respectively, showed no uniformity in amount of combined sulfur. In only one case, that of the p-nitrosodimethylaniline and aldehyde ammonia, did the coefficients fall closely together. In this case the difference was only about 5 per cent. In all the other cases, there was a wide variation in the coefficients; with the p-nitrosodimethylaniline the coefficient was 18.4 per cent greater, with the aldehyde ammonia 12.6 per cent greater, and with the thiocarbanilide 58.6 per cent greater than with the hexamethylenetetramine. In other words, the chemical state of cure was no index to the physical state of cure.

These four organic accelerators, though all reacting with sulfur during vulcanization, do not, when heated in xylene under similar conditions, form insoluble reaction products which seriously interfere with the determination of combined sulfur.

THE RELATIVE merits of the stress-strain relations and coefficient of vulcanization as measures of *state of cure* have been the subject of lively discussion for many years. As far back as 1902, Weber² stated that the fact that two different specimens of vulcanized rubber, even when produced from the same batch of crude rubber, possessed equal coefficients of vulcanization, by no means implied that the two specimens also possessed the same physical constants. It was his viewpoint that variations in the amount of working which a sample of rubber received and differences in the temperature and duration of the vulcanization period influenced the *physical result* of the vulcanization process, without exerting a corresponding influence upon the *chemical result*. Axelrod³ has presented figures which support Weber's view that the temperature of the vulcanization largely affects the physical properties. Upon vulcanizing to the same vulcanization coefficient, but at two different temperatures, Axelrod found marked differences in the load required to produce a given elongation in the two vulcanizates. Schidrowitz,⁴ in working out a systematic method for testing rubber and placing the "optimum cure" by means of "slope," came to the conclusion that the progress of vulcanization can be accurately expressed by a series of stress-strain curves, and the state of cure of a given mixing

at a given time by the corresponding curve. Stevens,⁵ on the other hand, while admitting that the coefficient of vulcanization can be taken only as an approximate guide to the condition or degree of vulcanization, favors this factor, rather than the physical properties, as a measure of state of cure, since the tensile properties of a vulcanized rubber are not constant, but vary with the age of the specimen, while the coefficient of vulcanization suffers little change under similar conditions; furthermore, according to Stevens, the coefficient of vulcanization is an index to the stability of the physical properties. Spence⁶ takes a similar stand as regards the value of the coefficient. Eaton and Grantham⁷ utilize the physical properties almost exclusively in their work on the variability of plantation rubber, though their figures⁸ for combined sulfur show a very marked relationship between physical and chemical properties. De Vries,⁹ though not finding such large differences as do Schidrowitz and Goldsbrough,¹⁰ agrees with the latter that the chemical process of the combination of rubber and sulfur is in itself quite independent of the physical process which determines the position of the stress-strain curve. De Vries' arguments are based on a series of age tests conducted at 75° C. from which he concludes that it is possible to bring the rubber to the "correct" or any chosen standard of cure (as judged by the curve) with other and quite arbitrary coefficients of vulcanization. He, therefore, is of the opinion that the mechanical properties are the more important, and that the curve is a better gage for judging the properties than is the chemical condition as expressed by the coefficient of vulcanization. Stevens¹¹ aptly replies to this that De Vries has only shown that *under different conditions* different coefficients of vulcanization may be obtained for the same rubber, giving the same stress-strain curve. Stevens is willing to admit the value of an arbitrary "standard curve" in placing state of cure, provided the results can be correlated to rubber correctly cured in the manufacturing sense, and "it is here that the coefficient is of great value."

From this review of the literature it appears that there is considerable confusion concerning the term "state of cure." It is the opinion of the writers that to cure two samples of rubber to the same *chemical state of cure* is one thing, while to vulcanize to equivalent *physical state of cure* may be quite another. The *physical state of cure* is vital for the performance of vulcanized rubber in service, provided of course that the stability of the physical condition is certain. It is here that the *chemical state of cure* unquestionably plays a major part. It would appear, from what has already been published, that only under standardized conditions of mixing, curing, and testing is there a close relationship between the *chemical and physical states of cure*.

¹ *J. Soc. Chem. Ind.*, **35** (1916), 872.

² *India Rubber J.*, **52** (1916), 861.

³ *J. Soc. Chem. Ind.*, **34** (1915), 989; **35** (1916), 715.

⁴ *Agr. Bull. Federated Malay States*, **27** (1918), 139.

⁵ *India Rubber J.*, **53** (1917), 101.

⁶ *Ibid.*, **51** (1916), 505.

⁷ *Ibid.*, **53** (1917), 220.

¹ Presented before the Division of Rubber Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² "The Chemistry of India Rubber," p. 93.

³ *Gummi-Ztg.*, **24** (1909), 352; *J. Soc. Chem. Ind.*, **29** (1910), 34.

⁴ *Rubber Industry (London)*, **1914**, 212; cf. *J. Soc. Chem. Ind.*, **34** (1915)

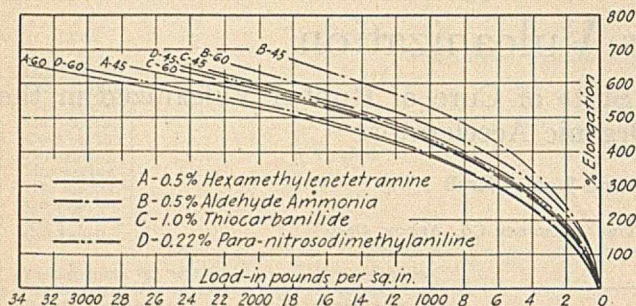


FIG. 1

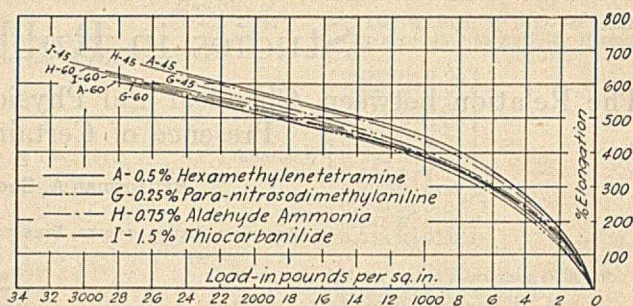


FIG. 3

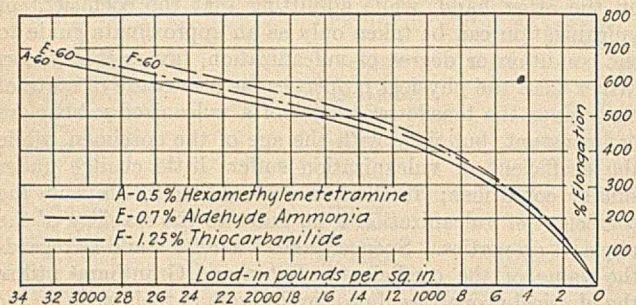


FIG. 2

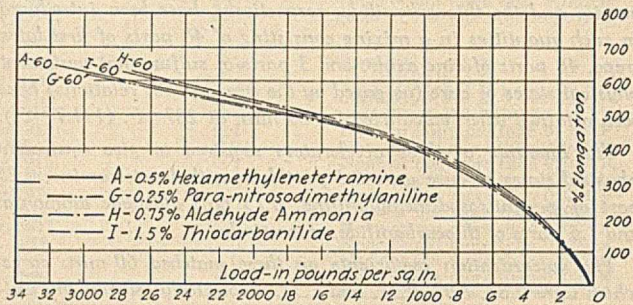


FIG. 4

With the advent of organic accelerators the relationship between the vulcanization coefficient and physical properties came to be more and more questioned. Cranor,¹² in curing smoked sheet compounded with 6 per cent of sulfur and 1 per cent zinc oxide, without accelerator and in the presence of hexamethylenetetramine and of dimethylammonium dimethyl-dithiocarbamate, respectively, found that when cured to practically the same coefficient of vulcanization (2.85, 2.83, and 2.68, respectively), the loads required to produce an elongation of 700 per cent were 700, 2070, and 2910, respectively. The periods of cure in these cases were all of different length: 130 min. at 292° F., 50 min. at 292° F., and 5 min. at 295° F., respectively. Furthermore, in spite of the moderate coefficient obtained in each case, Cranor stated that the 50-min. "hexa" cure was somewhat overvulcanized and that the 5-min. "carbamate" cure was much overcured. Similar results have been obtained when vulcanizing samples to the same coefficients with *p*-nitrosodimethylaniline.¹³

Viewing his results from the standpoint of constant physical properties, Cranor has shown that when the three stocks mentioned above were cured to the point where a load of 1000 lbs. per sq. in. was required to produce an elongation of 700 per cent, the respective coefficients were approximately 4.9 for the unaccelerated stock, 1.8 for the hexamethylenetetramine stock, and 0.9 for the stock containing the dimethylamine addition product. The coefficients of vulcanization were thus no index to the physical state of cure in this case.

In order to throw further light upon the relation between the chemical and physical states of cure in the case of accelerated stocks, the writers have investigated the behavior of hexamethylenetetramine, *p*-nitrosodimethylaniline, aldehyde ammonia, and thiocarbanilide, when introduced in such quantities that equivalent physical states of cure are obtained when cured for the same length of time at the same temperature. In this way each stock was subjected to identical heat conditions, which, from the above review of the work of pre-

vious investigators, appears to be of paramount importance if a fair comparison of stress-strain data and vulcanization coefficients is to be made. In matching the physical states of cure of these stocks, no attempt was made to work with the so-called "optimum cure." The cure selected was somewhat below that of maximum tensile strength (cf. the control stock A, Fig. 5) and was judged to be a good commercial cure.

EXPERIMENTAL PROCEDURE

COMPOUNDING—A selected batch of massed first latex crepe was used throughout the work and the mixing consisted of 48 parts of rubber, 48 parts of zinc oxide, and 3 parts of sulfur, to which was added the required amount of accelerator necessary to give, when cured for 60 min. at 287° F. (141.7° C.), a vulcanizate having stress-strain relations which would match those produced by using 0.5 part of hexamethylenetetramine (see Curve A-60, Fig. 1).

The selection of a formula with so high a percentage of zinc oxide (48 per cent by weight, 14 per cent by volume) may appear an unfortunate choice. The writers selected this for two reasons. In the first place, it was essential to work in the presence of zinc oxide, in order to bring out the full activity of at least two of the accelerators under consideration. In the second place, from the standpoint of comparing the results with certain actual compounds used in factory practice, it was desired to use a somewhat highly compounded stock. The writers are aware that this procedure, by flattening out the stress-strain curves and bringing those for successive cures nearer together, made the selection of identical stress-strain curves more difficult, at the same time complicating the analysis for combined sulfur.

The organic accelerators were all carefully tested for purity. The hexamethylenetetramine was the chemically pure material; the *p*-nitrosodimethylaniline melted at 83° to 84° C.;¹⁴ the aldehyde ammonia, melting at 93° to 95° C.,¹⁵ was so free from the resinous decomposition products with which it is commonly contaminated that it was easily ground to a

¹² *India Rubber World*, 61 (1919), 137.

¹³ Van Rossem, "Communications of the Netherland Govt. Inst. (Delft)," Part VI, p. 213.

¹⁴ Schraube gives melting point of pure material as 85° C.

¹⁵ Melting point variously given in the literature: Beilstein, 70° to 80°; Aschan, 96° to 98° C.

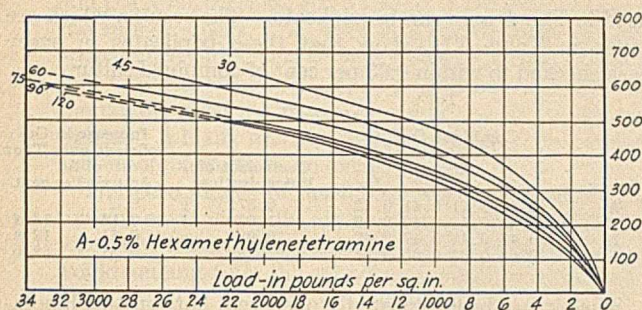


FIG. 5

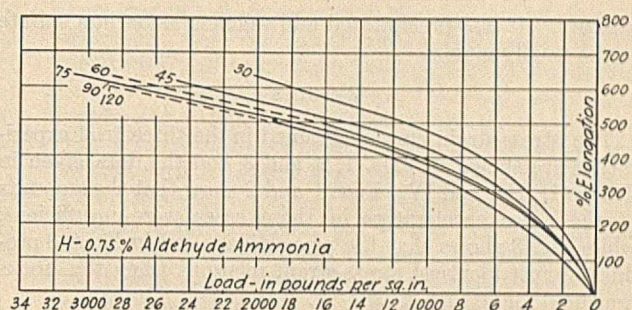


FIG. 7

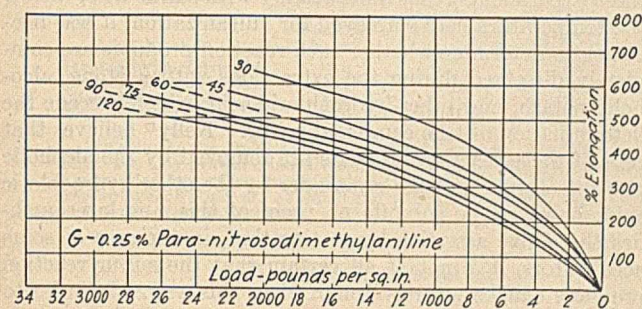


FIG. 6

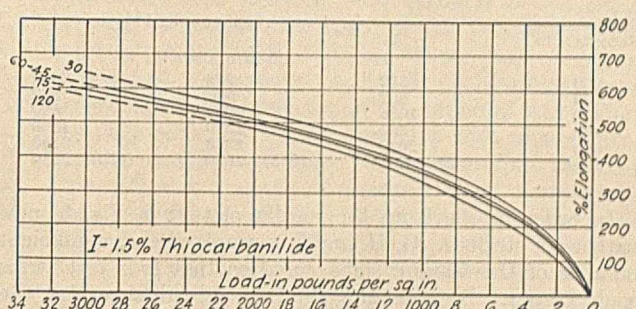


FIG. 8

fine powder; and the thiocarbanilide was twice recrystallized from alcohol and melted at 149° to 150° C.¹⁶

Three trial experiments were made before the amounts of these three accelerators were arrived at, which were necessary to give the same stress-strain curve in 60 min. at 287° F. as 0.5 part of hexamethylenetetramine.

The complete list of compounds investigated is given in Table I.

	TABLE I								
	CONTROL	EXPT. 1			EXPT. 2		EXPT. 3		
	A	B	C	D	E	F	G	H	I
First latex crepe....	48	48	48	48	48	48	48	48	48
Zinc oxide.....	48	48	48	48	48	48	48	48	48
Sulfur.....	3	3	3	3	3	3	3	3	3
Hexamethylene-tetramine.....	0.5
Aldehyde ammonia..	..	0.5	0.7	0.75	..
Thiocarbanilide....	1.0	1.25	1.5
p-Nitrosodimethylaniline.....	0.22	0.25

MIXING—The stocks were mixed on a small experimental mill. After milling for 10 min. to break down the rubber, the mixture of zinc oxide, sulfur, and accelerator was incorporated during the course of 4 min. and the mixing was continued for an additional 8 min. in order to obtain a uniform product. The mill rolls were cooled to approximately the same temperature before mixing each batch and kept the same distance apart for all mixes. After mixing, the stocks passed directly to a small calender where they were calendered to a thickness of approximately 0.1 in.

bath. This procedure was necessary to prevent reducing the temperature of the curing bath when inserting molds. After vulcanization, the molds were immediately plunged into a tank of cold water. The slabs produced were approximately 0.07 in. thick.

PHYSICAL TESTING—Dumb-bell strips were cut from the vulcanized slabs 0.25 in. wide at their central portion. The stress-strain data were obtained on the Scott testing machine by two observers. Strips of this thickness permitted the employment of the inner scale on the machine so that the load could be easily read to 0.4 lb. Two strips of each cure were broken except where otherwise stated.

ANALYTICAL METHOD—The combined-sulfur figures and vulcanization coefficients were determined in the following manner: 1-g. samples, creped on a tight cold mill, were extracted with acetone for 16 hrs. in an Underwriters extraction apparatus. After air-drying for about 15 min., the acetone-extracted samples were digested for 8 hrs. in a 5 per cent alcoholic potash solution, followed by a 16-hr. extraction with alcohol. After another air-drying, the samples were covered in a small flask with a mixture of 20 cc. ether and 20 cc. concentrated (aqueous) hydrochloric acid and allowed to stand at ordinary temperature for 1 hr. with occasional shaking. After a washing with hot water a final extraction was made with boiling water for 4 hrs. This procedure is similar to that of Kelly,¹⁷ the ether-hydrochloric acid treatment being that proposed by Stevens.¹⁸ The

PERCENTAGE ELONGATION	TABLE II							
	LOAD—LBS. PER SQ. IN.							
	A	B	C	D	A	B	C	D
200	235	166	213	205	324	212	254	290
300	470	302	467	465	605	392	508	610
400	825	510	790	810	1010	670	845	1025
500	1410	865	1300	1340	1720	1110	1380	1620
600	2240	1375	2080	2060	2680	1770	2120	2600
Break	(637) 2770	(675) 1840	(620) 2310	(650) 2460	(656) 3380	(640) 2180	(637) 2460	(637) ..

CURING—The curing was conducted at 287° F. (141.7° C.) in a paraffin bath regulated to within 0.5° F. The molds were allowed to remain in a preheating bath at approximately 320° F. for exactly 1 min. before they were placed in the curing

sulfur was determined in the extracted samples by the method of Waters and Tuttle,¹⁹ by oxidizing with nitric acid-bromine mixture and fusing with potassium nitrate-sodium carbonate

¹⁶ Lellman, 150.5° C.; Bamberger, 153° C.

¹⁷ THIS JOURNAL, 14 (1922), 196.

¹⁸ India Rubber J., 50 (1915), 187.

¹⁹ Bur. Standards, Reprint 174.

mixture. It was precipitated and weighed as barium sulfate in the usual manner.

RESULTS

The stress-strain curves obtained in the three trial experiments are shown in Figs. 1, 2, and 3, and the data given in Tables II, III, and IV. Figs. 1 and 2 show that the amounts of the three accelerators in these cases were insufficient, while Fig. 3 shows that the proportions used in Expt. 3 produce almost identical stress-strain relations when the stocks are cured for 60 min. at 287° F. (141.7° C.).

TABLE III

PERCENTAGE ELONGATION	LOAD—LBS. PER SQ. IN.			
	A	E		F
		60-Min. Cure		
200	372	308		340
300	602	540		550
400	1005	900		850
500	1660	1520		1380
600	2620	2380		2180
Break	(662) 3300	(675) 3080		(650) 2580

In order to check up the results plotted in Fig. 3, new batches of stocks A, G, H, and I were mixed and a sufficient number of the 60-min. slabs cured so that four test strips could be cut. By averaging the four individual results, the

TABLE IV

PERCENTAGE ELONGATION	LOAD—LBS. PER SQ. IN.									
	A	G			H	I	A	G	H	I
		45-Min. Cure					60-Min. Cure			
200	248	263	266	286	302	330	386	315	332	
300	455	560	464	464	605	620	685	595	652	
400	788	960	805	805	1030	1070	1130	1010	1070	
500	1325	1535	1420	1420	1670	1820	1870	1740	1750	
600	2090	2360	2170	2170	2650	2740	2660	2590	2580	
Break	(637) 2480	(600) 2360	(650) 2720	(637) 3080	(606) 2840	(605) 2720	(644) ..	(625)	

stress-strain curves plotted in Fig. 4 (data in Table V) were obtained.

TABLE V

PERCENTAGE ELONGATION	LOAD—LBS. PER SQ. IN.			
	A	G		H
		60-Min. Cure		
200	290	320	298	298
300	610	655	560	575
400	1020	1100	955	975
500	1740	1780	1610	1580
600	2760	2760	2480	2540
Break	(650) ..	(620) 3000	(630) 2940	(630) ..

The stress-strain data for these four stocks, over a range of cures from 30 to 120 min. (see Table VI), are plotted in Figs. 5, 6, 7, and 8. These are introduced in this report merely to give a more complete picture of the general characteristics of these stocks.

The combined sulfur determinations on the 60-min. cures

used in Fig. 4 were run in triplicate. The results, which are given in Table VII, show that these triplicates in every case checked to within 0.03 per cent of combined sulfur.

TABLE VII

Stock	Combined Sulfur Per cent Sample				Coefficient of Vulcanization	Increase in Coefficient over That of A	
	1	2	3	Av.		Actual	Per cent
A	0.44	0.41	0.41	0.42	0.87
G	0.50	0.51	0.49	0.50	1.03	0.16	18.4
H	0.47	0.48	0.47	0.47	0.98	0.11	12.6
I	0.66	0.65	0.66	0.66	1.38	0.51	58.6

Since it has been repeatedly observed, both in this laboratory and elsewhere,²⁰ that the organic accelerators used in these experiments react quite readily with sulfur at or below the temperature here employed for vulcanization, it was necessary to determine whether such reaction products are completely dissolved during the extractions with acetone, alcoholic potash, and ether-hydrochloric acid, which precede the determination of true combined sulfur. Kelly¹⁷ believes that part of these reaction products are removed by the alcoholic potash solution and the remainder by the ether-hydrochloric acid; however, he submits no proof of this, and later qualifies the above assertion by stating that, in the case of some accelerators, it is not at all certain that the sulfur reaction products can be entirely removed in this way. In order to

throw some light on this point in the case of the four accelerators under consideration, they were heated with sulfur and zinc oxide under conditions approaching as closely as possible those employed during the actual vulcanization. The same proportions of zinc oxide, sulfur, and accelerator, as employed in compounding the above stocks (A, G, H, and I), with xylene²¹ (boiling point 141° C.) replacing the rubber, were heated for 60 min. at 287° F. (the time and temperature actually employed in the vulcanization). At the end of this time, the xylene was distilled off under reduced pressure

²⁰ Peachey, Brit. Patent 113,570 (1918); Dubosc, *India Rubber World*, 59 (1910), 248; Bedford and Scott, *This Journal*, 12 (1920), 33; 13 (1921), 1034.

²¹ The writers are aware that, in changing from a colloidal medium (rubber) to a noncolloidal medium (xylene), the amounts of the various reaction products obtained from any given accelerator and sulfur may be differently proportioned. It would hardly be expected, however, that the nature of the reaction products would be changed.

TABLE VI

PERCENTAGE ELONGATION	LOAD—LBS. PER SQ. IN.								
	A	G		H	I	A	G	H	I
		30-Min. Cure					75-Min. Cure		
200	..	244	170	..	342	450	338	347	
300	400	428	410	607	765	822	638	750	
400	682	714	680	1040	1290	1340	1110	1210	
500	1150	1130	1125	1680	2135	2140	1780	1940	
600	1820	1785	1800	2590	2750	3100	
Break	(637) 2180	(637) 2070	(637) 2050	(644) ..	(620) ..	(562) 2740	(625) 3100	(612) ..	
		45-Min. Cure					90-Min. Cure		
200	274	292	270	290	418	565	321	..	
300	525	610	520	695	855	950	670	..	
400	885	1030	895	1160	1390	1490	1100	..	
500	1460	1620	1470	1800	2210	2310	1800	..	
600	2290	..	2340	2730	..	
Break	(637) 2790	(575) 2230	(619) 2500	(631) ..	(600) ..	(575) ..	(612) 2880	..	
		60-Min. Cure					120-Min. Cure		
200	315	342	292	290	487	625	430	470	
300	608	730	597	684	920	1020	765	865	
400	1035	1190	1000	1168	1460	1630	1210	1350	
500	1800	1870	1610	1860	2300	2600	1920	2160	
600	2900	2900	
Break	(637) ..	(587) ..	(631) ..	(637) ..	(581) ..	(525) ..	(600) ..	(600) ..	

and the resulting mass given the same extraction treatment as the rubber stocks, *i. e.*, with acetone, alcoholic potash, and ether-hydrochloric acid. The insoluble residue at the end of this treatment was collected on a Gooch crucible, washed thoroughly with hot water, and dried at 50° C. to constant weight. A blank was also run to determine the hydrochloric acid-insoluble in the zinc oxide.

The percentages of insoluble residue, after correcting for the zinc oxide-insoluble, are given in Column 1 of Table VIII, together with the figures showing what this insoluble material would amount to in the actual vulcanizates (Column 3).

TABLE VIII

ACCELERATOR	Insoluble Residue Formed Per cent	Accelerator in Stock Per cent	Insoluble ¹ in Stock Per cent	Stock
Hexamethylenetetramine	4.3	0.5	0.02	A
<i>p</i> -Nitrosodimethylaniline	11.0	0.25	0.03	G
Aldehyde ammonia.....	5.8	0.75	0.04	H
Thiocarbanilide.....	2.0	1.5	0.03	I

¹ Owing to the small amounts obtained in each case, the presence of sulfur was only proved qualitatively; the figures cannot, therefore, be used as correction factors for the vulcanization coefficients; but since the amounts present in each stock are so small and so nearly identical, the effect on the coefficient is almost negligible.

DISCUSSION OF RESULTS

The results for combined sulfur recorded in Table VII indicate that for accelerated stocks, even when the quantity of accelerator is so chosen that equivalent stress-strain relations are obtained in the same time of cure, the vulcanization coefficients show no corresponding uniformity. This lack of uniformity in the coefficients cannot be ascribed to sulfur retained in chemical combination by the respective accelerators, as the figures in Table VIII show. In other words, then, the vulcanization coefficient of an accelerated stock is no criterion of the physical state of cure. It is interesting in this connection to note the comments of Twiss²² along this line:

The chemical action of sulfur on the rubber induces the physical alterations which constitute the advantage to be gained by vulcanization, but the chemical and physical processes are not necessarily strictly proportionate and some accelerators influence one more than the other. In the presence of certain accelerators the physical or mechanical alteration is disproportionately rapid, and the tensile strength attains its maximum at a coefficient of vulcanization well below the normal value.

The coefficients recorded in Table VII are all remarkably low. Other investigators, however, have recorded similar results.²³ Kelly has given figures for a thiocarbanilide stock, having a combined sulfur content of only 0.84 and a coefficient of 0.99; the physical properties of this stock, however, are not recorded. Cranor found a stock to have satisfactory physical properties with a vulcanization coefficient of 1.09; he was working, however, with the very active dimethylammonium dimethyl-dithiocarbamate, and the curing time was only 3 min.

Looking at the results from another angle, they indicate that an accelerator has a specific action in vulcanization, aside from its influence on the chemical combination between rubber and sulfur. Many of the published figures on the properties of accelerated stocks show abnormally high tensile properties for low coefficients of vulcanization. However, in most cases, it is difficult to draw any conclusion as to any specific effect of the accelerator on the vulcanization process, since the duration of the curing period has been so variable. Many have ascribed these abnormal properties entirely to the

shortening of the curing period through the influence of the accelerator. By the tabulation of Gottlob's²⁴ results obtained with Vulkazit,²⁵ Seidl²⁶ has shown that the shorter the time of vulcanization, the higher the tensile strength corresponding to a definite combined sulfur content. Seidl states that, parallel with the strengthening of the rubber through the taking up of sulfur, a depolymerization of the rubber takes place under the influence of the heat which exerts its harmful effect to a lesser extent, the shorter the time of heating.

Aside from a theoretical interest, the results recorded in the present paper have a practical application, since for several commercially applicable accelerators, the quantities necessary for the production of equivalent *physical* states of cure have been derived. The problem of matching the physical properties of a stock in the presence of different accelerators, but under identical temperature conditions and duration of curing period, is one often confronting the rubber technologist, for shortening of the period of cure is far from the only consideration in connection with organic accelerators. Toxicity, volatility, miscibility, effect on range of cure, influence on aging properties,²⁷ and tendency to produce "scorching," all have an important bearing in the selection of accelerators for specific purposes. Furthermore, where a given stock, of definite stress-strain relations, has proved through years of experience in service its applicability for a specific purpose, the introduction of a new accelerator should not disturb these stress-strain relations unless exhaustive practical tests have proved the desirability of making such a change in these factors. Hence the value, in making comparative studies of accelerators, of matching physical "state of cure" and studying the relative behavior of stocks which contain *equivalent accelerating quantities* of accelerator.

The equivalent quantities which have been determined in the course of this work indicate that 1 part of hexamethylenetetramine is equivalent in accelerating power to 1.5 parts of aldehyde ammonia, 3 parts of thiocarbanilide, and 0.5 part of *p*-nitrosodimethylaniline, respectively, *in the type of stock here tested*. It does not follow, for example, that these exact relationships will hold for a stock in which the sulfur content is sharply reduced. As Twiss²⁸ has remarked, "the possibility must always be borne in mind that the activity of an accelerator may possibly be influenced by the proportion of free sulfur simultaneously present." Recent publications on the mechanism of the action of organic accelerators²⁹ would indicate that the concentration of sulfur is an important factor in their activation. Furthermore, it must not be understood that these equivalent quantities have been worked out to the limit of accuracy. Averaged stress-strain data indicate that the errors in curing and testing run upwards to 5 per cent, while the deviations of the three 60-min. stress-strain curves from the control (the 60-min. hexamethylenetetramine curve) average 7 per cent (cf. Fig. 4 and Table V). Further refinements of the equivalent quantities, though desirable from a theoretical standpoint, have not yet been made; from the standpoint of practical application, the above results are sufficiently accurate.

In a recent article entitled "The Relative Activity of Certain Accelerators in the Vulcanization of Rubber," Endres³⁰ arrived at somewhat different conclusions regarding the relative equivalent accelerating quantities of some of these same

²⁴ *Gummi-Ztg.*, **30** (1916), 303.

²⁵ Probably aldehyde ammonia.

²⁶ *Gummi-Ztg.*, **34** (1920), 797.

²⁷ Dittmar, *Z. angew. Chem.*, **34**, Aufsatzteil (1921), 465; *C. A.*, **16** (1922), 174.

²⁸ *J. Soc. Chem. Ind.*, **39** (1920), 125T.

²⁹ Bedford and Sebrell, *THIS JOURNAL*, **13** (1921), 1034; Bruni and Romani, *India Rubber J.*, **62** (1921), 63.

³⁰ *Caoutchouc & gutta-percha*, **18** (1921), 11089.

²² *J. Soc. Chem. Ind.*, **39** (1920), 125T.

²³ Cranor, *Loc. cit.*; Whitty and Smith, paper presented before the Section of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921; Kelly, *Loc. cit.*

accelerators. The activity of 1 per cent of hexamethylenetetramine, for example, was stated to be equivalent to that of 2.5 per cent of thiocarbanilide. It is interesting to note how he arrived at these figures. Discarding without any experimental evidence the coefficient of vulcanization as a measure of state of cure, since it "presents considerable variations," Endres uses the maximum physical properties as the criterion of correct cure, *i. e.*, the maximum tensile strength (or tensile product) at break. He states that he uses the stress-strain curves to obtain supplementary information. In the case cited above this latter was apparently overlooked, as the following figures for the equivalent cures will indicate:

ELONGATION	1 Per cent Hexamethylenetetramine 50-Min. Cure at 145° C. Load in Lbs./Sq. In.	2.5 Per cent Thiocarbanilide 50-Min. Cure at 145° C. Load in Lbs./Sq. In.
100	185	114
200	333	228
300	556	458
400	964	725
500	1700	1140
600	2800 (break)	1980
675	...	2660 (break)

Endres' results are further invalidated by the fact that the hexamethylenetetramine stock (above) contains 6 per cent of sulfur (to the rubber), while the thiocarbanilide stock contains 8 per cent. It is difficult to understand how a logical comparison can be drawn under such circumstances.

Quantitative Determination of Anthraquinone^{1,2}

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A method has been developed by which anthraquinone may be determined quantitatively in mixtures containing also phenanthraquinone, anthracene, phenanthrene, phthalic anhydride, phthalic acid, or other oxidation products of anthracene or phenanthrene.

The method consists essentially of reducing the anthraquinone to the red oxanthranol using zinc powder and 5 per cent solution of sodium hydroxide. The red solution is filtered in vacuum and titrated with standard potassium permanganate.

A detailed outline for carrying out the analysis is given, together with several representative results showing the accuracy of the method.

IN A PAPER from the Color Laboratory by H. F. Lewis³ a method is described by which anthraquinone may be determined quantitatively and with a fairly high degree of accuracy. While this method seems to be theoretically good, the authors have found it very troublesome because of the great length of time consumed in filtering and thoroughly washing the finely divided anthraquinone.

Grabe and Liebermann⁴ found that by the reduction of anthraquinone with zinc dust and dilute sodium hydroxide, a red compound to which they gave the name of oxanthranol, or anthrahydroquinone, was formed. This compound, which is soluble in the solution of sodium hydroxide, is very readily reoxidized to anthraquinone. Since the reduction to oxanthranol and the subsequent oxidation back to anthraquinone are quantitative, these reactions formed the basis for Lewis's method of determining anthraquinone. Lewis's method as outlined consists essentially of first reducing the anthraquinone with zinc and a 5 per cent solution of sodium hydroxide to the red oxanthranol, then reoxidizing it by shaking in air and weighing the anthraquinone recovered.

As already stated, the chief difficulty encountered in this process was the filtering of the recovered anthraquinone from the alkaline solution because the finely divided precipitate invariably clogged the pores in the asbestos mat of the Gooch crucible. In several of our experiments the time required for filtering alone was nearly a day.

In the modified method this filtering is eliminated and the red solution of oxanthranol is titrated with standard potassium permanganate, thus determining the anthraquinone volumetrically instead of gravimetrically as in the older methods. But as the oxanthranol solution is readily oxidized in air, the titration with potassium permanganate must be done in a vacuum or in the presence of an indifferent gas or vapor. It was therefore necessary to design a special apparatus for this purpose. The filtering tube, a somewhat magnified diagram of the construction of which is shown in Fig. 1A, was approximately 3.5 cm. inside diameter and 24 cm. long, and drawn down to a diameter of about 5 mm. On the bottom of this tube were placed an ordinary Witte filter plate, A, ground down to fit inside the glass tube, and an asbestos mat, B, $\frac{1}{16}$ in. thick, which was held in place by a 100-mesh brass gauze, C. Several dents were made in the wall of the tube just above the brass gauze to keep it in place, when the stirrer was set in motion. As brass is affected very little by alkali, one gauze would last through a large number of runs. The reducing and filtering tube was made of heavy pyrex glass.

The following procedure for making an analysis has given very satisfactory results, and it can be completed in about a half hour:

Weigh out 0.5000 g. of a very finely ground sample and mix this with 3 or 4 g. of zinc dust. The finer the sample and the more thoroughly it is mixed with the zinc dust, the more readily reduction takes place. A good way is to mix the sample and the zinc dust in an agate mortar, and stir the mixture until no yellow particles or streaks of anthraquinone are visible.

From the mortar, if one is used, transfer the dry mixture to a small beaker (150 to 200 cc.). Pour in about 100 cc. of boiling 5 per cent solution of sodium hydroxide and allow the solution to stand with occasional stirring for about 5 min. The temperature of this solution should be a trifle below the boiling point of the mixture, and the heating should not be continued too long. Too long heating results in the formation of some anthranol⁵ which contains one oxygen atom less than does the oxanthranol.

Run through the filter enough water that has previously been boiled and allowed to cool somewhat to form a layer about an inch deep in the bottom of the suction flask. Evacuate the suction flask until the air has been completely displaced by water vapor. The purpose of this is to sweep out all the air from the apparatus, thus obviating any oxidation of the red solution by oxygen other than that obtained from the potassium permanganate.

¹ Received May 31, 1922.

² Contribution No. 62 from the Color Laboratory. Published with the permission of the Department of Agriculture.

³ THIS JOURNAL, 10 (1918), 425.

⁴ Ann., 160 (1871), 126.

⁵ Liebermann and Gimel, Ber., 20 (1887), 1854.

Pour the red solution, together with the zinc dust and unchanged anthraquinone, into the reducing and filtering tube (Fig. 1, C), which should be kept hot by means of the electric heater D. If a rheostat is placed in the circuit the temperature of the heater can be kept very constant at about 90° to 95° C., which is about right for the best results.

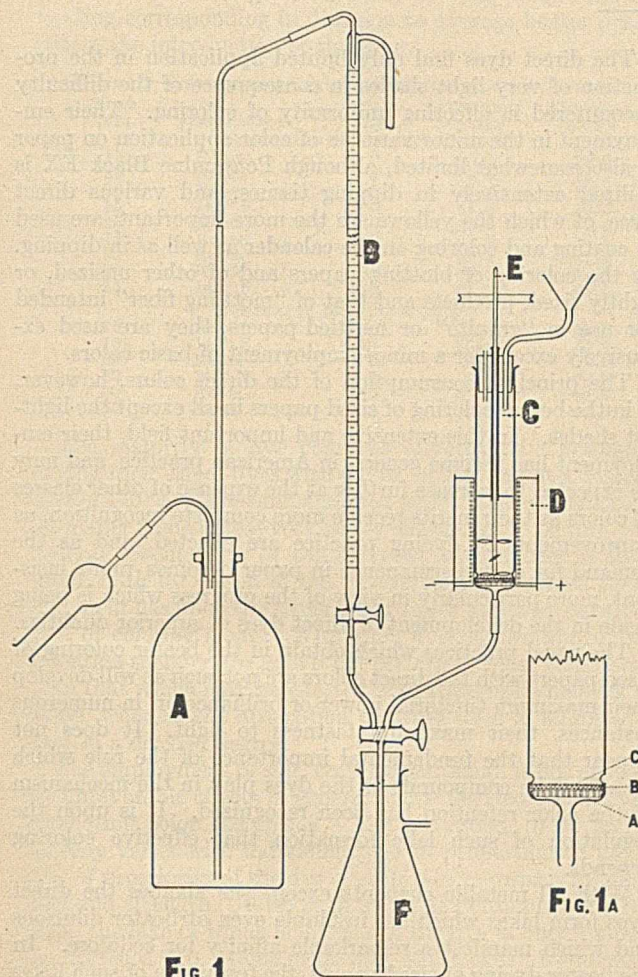


Fig. 1

Fig. 1A

A—KMnO₄ BOTTLE
B—BURET
C—REDUCING AND FILTERING TUBE
D—ELECTRIC HEATER
E—STIRRER
F—SUCTION FLASK

In filtering, care must be taken that no air is drawn into the filter flask. This is best accomplished by always leaving a small quantity of the solution in the filter tube. In order that the surface of the solution might be seen while filtering, the electric heater was held in place by a clamp fastened to a ring stand, and could thus be raised or lowered at will.

If care is exercised during filtration, two layers will form in the suction flask. This is highly desirable, inasmuch as the water already in the flask, which forms the upper layer, has been boiled free from dissolved air, thus protecting the red solution from any action of atmospheric oxygen.

Usually three or four reductions are sufficient, although unless the sample is very finely powdered six or eight may be necessary. The reduction must be continued until no more red solution is formed in the reducing tube after heating and stirring for about 5 min.

When the reduction has completed, fill the reducing and filtering tube approximately half full with the hot sodium hydroxide solution. After each increment of the titrating solution has been drawn into the filter flask, turn the two-way stopcock so as to admit some of this alkaline solution to wash out the potassium permanganate solution lodged in the tube between the stopcock and the solution in the flask.

The potassium permanganate used was prepared by dissolving 3.8 g. per liter and allowing the solution to stand for several days. The standardization of this solution was accomplished by grinding 0.5000 g. of pure anthraquinone to an impalpable powder and thoroughly mixing it with zinc dust. The reduction was then carried out as previously described.

The presence of phenanthraquinone with the anthraquinone does not interfere with the determination of the latter. Several runs were made in which anthraquinone and phenanthraquinone were mixed in different proportions, but in every case the results obtained were well within the limits of experimental error. It should be noted at this point that if the sample contains only pure anthraquinone, as when standardizing the potassium permanganate solution, the end-point is reached when the solution in the filter flask becomes perfectly colorless. Upon the addition of more titrating solution the color changes to a dark green, owing to the formation of potassium manganate (K₂MnO₄). If phenanthraquinone is present, the solution has a slightly bluish green tinge for the end-point, which upon addition of more potassium permanganate solution changes to a brownish green color, becoming darker. This color change probably may be explained by assuming that a derivative of phenanthraquinone analogous to oxanthranol is formed by the action of zinc and sodium hydroxide solution, and that this compound is not as readily oxidized back to phenanthraquinone as oxanthranol is to anthraquinone. From the results obtained, after having made scores of determinations of anthraquinone in mixtures containing also phenanthraquinone, anthracene, phenanthrene, phthalic anhydride, and phthalic acid, together with other oxidation products of anthracene and phenanthrene, it has been observed that there is a distinct change in color of the solution in the suction flask after sufficient titrating solution has been run in to oxidize all the oxanthranol.

Table I, showing a few results obtained on mixtures of anthraquinone and phenanthraquinone, will give an idea of the degree of accuracy obtainable with this method.

TABLE I

Weight of Anthraquinone Grams	Weight of Phenanthraquinone Grams	Proportion of Anthraquinone Per cent	KMnO ₄ Solution Cc.	Anthraquinone Determined Per cent	REMARKS
0.5000	0.0000	100.00	37.85	100.00	Blank. Standardization
0.4750	0.0250	95.00	36.00	95.11	
0.4500	0.0500	90.00	34.00	89.83	
0.4250	0.0750	85.00	32.20	85.07	
0.4000	0.1000	80.00	30.30	80.06	
0.4000	0.1000	80.00	30.22	79.81	
0.3750	0.1250	75.00	28.32	74.82	
0.3500	0.1500	70.00	26.40	69.75	
0.2000	0.0000	100.00	29.1	100.00	Blank. Different KMnO ₄
0.2000	0.1000	66.667	29.1	66.667	

The observed and calculated percentages of anthraquinone agree very well. Equally good agreements were readily obtained on check runs of the same sample, thus making duplicate determinations almost unnecessary.

In Lewis's method the anthraquinone was dissolved in a small quantity of alcohol. This is not permissible in the author's modification, for the reason that the alcohol would be oxidized to acetaldehyde in the titration with the potassium permanganate solution, thus causing the results to run high.

If the precautions outlined are observed in detail the average analyst should experience no difficulty in obtaining concordant results by this method which will save much time.

Application of the Direct Dyes in Coloring Paper¹

By Walter C. Holmes

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With paper materials in general, the best results in dyeing direct dyes in sized papers are obtained when provision is made to insure maximum retention in the form of dye and the precipitation of residual color in the form of some lake other than the aluminium lake. The color should be dyed with salt, the amount of alum used in sizing reduced to a minimum, and the addition of the alum preceded by that of calcium chloride or other suitable metallic salt, which will precipitate a lake of comparatively desirable characteristics.

With ground wood furnishes, on the other hand, the best results are obtained if the absorption of the dye is prevented entirely by preceding the addition of the color by that of the metallic salt which is most suitable.

In the dyeing of mixed furnishes containing ground wood, the same principles of color application should be followed in conjunction with the customary provisions for insuring uniformity of coloring.

The methods outlined will increase the brightness of the dyeings without incurring the disadvantages attendant upon the employment of basic dyes in conjunction with direct dyes.

By means of the employment of copper sulfate in the case of numerous individual dyes and dye combinations, a considerable range of good shades of great fastness may be obtained.

THE DIRECT, or substantive, dyes are soluble sodium salts of various color acids, characterized by an affinity for cellulose which is sufficiently strong to render practical their application in coloring paper materials without the intervention of precipitating or mordanting agencies. Their employment, accordingly, is peculiarly advantageous in coloring unsized, or lightly sized, papers and such products as "mottling fiber." The same property, on the other hand, restricts their utility in certain respects, and necessitates suitable precaution in their general application.

They are further differentiated from dyes of other classes by the relative insolubility of the lake compounds which they form in beater operation and the pronounced affinity of the latter for cellulose.

As a class, they are characterized by comparatively excellent fastness to light and by tinctorial strength and brightness of shade which are only moderate. A minor disadvantage attendant upon their employment is a tendency to mottled effects. The solubility, the completeness of color retention, with the accompanying advantage of freedom from color in back-waters, and the relatively slight tendency to result in two-sided effects in the sheet, are excellent.

In addition to characteristics common to the class, individual dyes possess, in numerous instances, distinctive qualities which make them of special value for paper application. The unique and complete stability of Pontamine Yellow SX and Pontamine Yellow CH to the action of hypochlorites; and the extreme resistance of the latter to alkali, whereby it is exceptionally qualified for employment in coloring papers in which soaps are to be wrapped, may be cited by way of example.²

¹ Presented before the Division of Dye Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² Such individual properties of the direct dyes, as well as those of colors of other classes, as are of essential interest to the paper manufacturer have been compiled in a chart to be included in a chapter on "The Coloring of Paper" in a vocational-educational textbook which will receive early publication by the American Pulp and Paper Association.

The direct dyes find only limited application in the production of very light shades in consequence of the difficulty encountered in effecting uniformity of coloring. Their employment in the minor varieties of color application on paper is also somewhat limited, although Pontamine Black EX is utilized extensively in dipping tissues, and various direct dyes, of which the yellows are the more important, are used in coating and coloring on the calender as well as in dipping. In the coloring of blotting papers and of other unsized, or lightly sized, products and that of "mottling fiber" intended for use in "granite" or mottled papers, they are used exclusively except for a minor employment of basic colors.

The principal consumption of the direct colors, however, is in the beater coloring of sized papers in all except the lightest shades. In this extensive and important field, their employment has become general in American practice, and may be expected to increase further at the expense of other classes of colors as their merits receive more complete recognition, as improvements in dyeing practice are effected, and as the demand for color permanence in paper becomes more insistent, more particularly in view of the progress which is being made in the development of direct dyes of superior qualities.

The usual practices which obtain in the beater coloring of sized papers with the direct colors are not such as will develop their maximum tinctorial power or brilliance or, in numerous instances, their maximum fastness to light. It does not appear that the fundamental importance of the role which metallic lake compounds of the dyes play in the mechanism of the color retention has been recognized. It is upon the regulation of such lake formation that effective coloring depends.

With all metallic elements except the alkalies the direct dyes form lakes which are insoluble even at beater dilutions and which manifest a remarkable affinity for cellulose. In the beater dyeing of sized papers, the formation of such lakes is unavoidable since it is impossible to effect complete absorption of the dye by the stock. Both dye and lake contribute to the total coloring effect obtained. The essential mechanism of the dyeing is that of a limited absorption of the dye itself (the soluble sodium salt of the color acid), followed by the precipitation upon the stock of such portions of the dye as remain in the liquor, in the form of the aluminium lake (the insoluble aluminium salt of the color acid), upon the addition of the alum required in the sizing. The total percentage retention of the color is very high, except when very heavy shades are run, but that factor alone is not decisive in evidencing the efficiency of the practice. The true effectiveness of the dyeing is dependent upon the degree in which the color is retained in the more advantageous form, which is, invariably, that of the dye.

When dyed in the form of dye the color is superior in both tinctorial strength and in brightness of shade, in degrees which are variable with different dyes but which are usually of a material order. With certain exceptions, into which other considerations enter, which will be noted subsequently, it is essential in obtaining optimum results, therefore, that the retention of the color should be in the form of dye, so far as may be possible, with a minimum degree of lake formation; and the effectiveness of any dyeing practice must be rated on the basis of the degree in which that condition is obtained. In ordinary trade practice, wherein no provision is made to

increase the absorption of the dye, less than one-third of the color present in dyeing 6-lb. shades is generally absorbed as such and escapes precipitation in lake form.

Quantitative data on the absorption of two representative direct dyes in 6-lb. shades with bleached sulfite and ground wood furnishes are given in Table I. The stock received a beating corresponding in duration to average beater practice before the introduction of the color.

TABLE I—PERCENTAGE COLOR RETENTION IN 6-LB. DYEINGS

TIME Min.	Temperature	Salt Lbs.	BLEACHED SULFITE EX CONC.	GROUND WOOD
PONTAMINE BLACK				
15	Room	0	30.4	25.5
30	Room	0	29.6	24.2
60	Room	0	31.5	27.0
15	140° F.	0	44.6	50.5
15	Room	40	58.8	61.3
15	Room	80	67.3	65.7
30	Room	40	56.5	61.5
30	Room	80	67.2	68.3
15	140° F.	40	64.2	68.6
PONTAMINE SKY BLUE 5BX				
15	Room	40	63.5	50.8
15	140° F.	40	50.8	38.1
30	Room	0	25.4	28.6
30	140° F.	0	...	19.0
30	Room	40	68.3	60.3
30	Room	80	70.0	60.8

The majority of dye concerns advocate the practice of dyeing their direct dyes with 40 lbs. of salt and at a temperature of 140° F.; a recommendation which is usually ignored by the paper trade unless very heavy shades are to be run. The general specification of the elevated temperature is ill advised, both by reason of the deleterious effect which its employment has upon the sizing of the paper and from consideration of coloring alone. With such dyes as are improved in retention thereby, the gain is not materially more considerable than that which may be effected with the employment of salt alone, whereas the absorption of other dyes is inhibited by heat in a decided degree.

The employment of salt, on the other hand, is not attended by unfavorable effects in general and is decidedly effective in promoting color absorption. The advantage to be derived thereby varies with individual dyes in proportion to the degree of superiority of the dye over its lake in respect to brightness and strength. With such colors as Pontamine Sky Blue 5BX, the lake of which is inferior to the dye in only a moderate degree, a 6-lb. dyeing made with 40 lbs. of salt is equivalent in strength to a 7-lb. dyeing without salt, and is decidedly brighter. With Pontamine Fast Pink BL, which is typical of dyes which are more seriously affected by conversion into their aluminum lakes, a 6-lb. dyeing with 40 lbs. of salt is fully equivalent in strength to a 9-lb. dyeing in general practice, and is brighter to an extreme degree.

The improvement in strength and brilliance cited, together with an attendant minor advantage of a more complete retention of color in heavy shades, is entirely consequent upon the limitation of lake formation which the employment of salt effects. A further improvement, which is material in degree with the majority of direct colors, may be effected by modification of the character of lake formation. The aluminum lakes of the dyes have particularly unfavorable characteristics. With the great majority of colors the calcium, barium or magnesium lakes are decidedly brighter and more attractive in shade, while even the iron lakes are often appreciably superior to those formed with alum. It is due to these facts that the presence of mineral impurities in the beater, such as may occur in the water or find introduction in the stock, is beneficial rather than otherwise in its influence on the shades obtained in dyeing sized papers with direct dyes in the usual practice. It should be noted, incidentally, that the preliminary addition of alum to the beater in order to effect the removal of such mineral impurities is, therefore, decidedly injudicious in so far as regards its influence on the shades obtainable with the direct colors.

The best results in dyeing the direct dyes in sized papers, therefore, are obtained only when provision is made which insures a maximum color retention in the form of dye and a precipitation of residual color in the form of such metallic lakes as are most suitable in the case of the individual dyes. As a general practice, it may be recommended that the calcium lakes be utilized, and that precipitation be effected by means of the addition of suitable amounts of calcium chloride. A subsequent addition of alum is essential in obtaining the best results in respect to sizing, but the amount of alum employed, which will be less than is normally necessitated, should be restricted so far as is possible. By compliance with the principles of color application outlined above, results are obtained which are, in general, greatly superior to those obtained in usual practice.

A limited number of direct dyes which find application on paper exhibit a decided susceptibility to such conditions of acidity as obtain in the paper beater in usual practice; with such it is customary to advocate the employment of limited amounts of soda ash. An excess of soda ash over the amount required to neutralize the acidity of the alum is attended by serious interference with the satisfactory sizing of the paper, and by color losses consequent upon the instability of the color lake to alkalis, but the use of restricted quantities has no more serious consequences than a possible increase in frothing. With colors of this type the improvement effected by the employment of salt and calcium chloride is of about the same order as that obtained by a resort to the use of soda ash. It is probably impossible to employ such dyes in the beater coloring of sized papers in such manner as to develop their maximum excellence of shade without entailing some measure of disadvantage in certain other respects. It is fortunate that their employment is becoming less necessary by reason of the increasing availability of dyes of similar shade and superior qualities.

GROUND WOOD FURNISHES

The general practice advocated for the direct colors is not recommended in the coloring of ground wood furnishes, wherein certain particular considerations enter. The phenomenon of color absorption in the form of dye is not one in which mere surface deposition of color is the entire, or even the predominant, component, but involves a decided degree of penetration of color within the fiber substance, whereas the dye lakes are deposited upon the fiber surface. In the particular instance of ground wood, it is found that the opacity of the stock operates to mask and obscure such portions of the dye as have become deposited within the fiber. With yellow dyes the effect observed is not pronounced, but the impairment in tinctorial strength and brightness of direct dyes, in general, is very material. In dyeing Pontamine Sky Blue 5BX, for example, in 6-lb. shades upon bleached sulfite and ground wood furnishes, it is found that the depth of shade developed on the bleached sulfite stock is several times greater than upon the ground wood, although there is no material difference in the amount of dye actually absorbed. It is possible to obtain shades of better brightness and of considerably greater depth in the case of ground wood by dyeing in the form of lake.

In the coloring of ground wood furnishes, therefore, it is advantageous, in general, to obtain color retention in the form of some suitable lake with the entire avoidance of absorption of the dye itself, as may easily be effected by the addition of a suitable amount of calcium chloride, or other metallic salt, prior to the introduction of the dye. The dyeings obtained thereby are brighter and stronger, in a degree which varies with the color and absorption characteristics of individual dyes and, in some measure, upon the amount of color employed, but which is generally considerable.

MIXED FURNISHES

In the dyeing of mixed furnishes containing ground wood, wherein difficulty is encountered in effecting uniformity of coloring in consequence of the decided difference in depth of shade obtained with ground wood and with the other ingredient materials under identical dyeing conditions, the general manipulation of the customary practice should be followed. The ground wood should be introduced into the beater and receive a preliminary and partial coloring before the other stock and the remainder of the color are introduced, or the greatly preferable course of a dyeing in separate beaters with a subsequent combining of the stocks followed when the necessary equipment is available. In either case, however, the general provisions which have been outlined as essential to the effective coloring of the separate stocks should be followed. It will not be found possible to obtain complete effectiveness in coloring if it is necessary to carry out the dyeing in a single beater. The best results possible in that case are obtained by adding the ground wood, a suitable amount of mineral salt, a portion of the color, the remaining stock, the remainder of the color, salt, and a second suitable amount of mineral salt, size, and alum in the order given. The operation is not essentially more complicated than the usual practice in such cases and will give decidedly better dyeings in respect to strength and brightness. The degree of uniformity of coloring effected will be dependent, as it is in the more usual practice, upon the correct determination of the proportion of the color which is to be added at the beginning of the dyeing.

These methods which have been advocated for the application of the direct dyes are found to have an influence which is very slightly favorable, rather than otherwise, upon the stability of the dyed product to photochemical action. On the other hand, the employment of basic colors in conjunction with direct colors affords, at best, products of only moderate stability to light, and may result, under unfavorable circumstances, in products of but slight fastness, in color losses, and in variations in shade. The lake compounds of direct and basic dyes are not of superior characteristics when formed under the most favorable conditions, while compounds are formed, in other circumstances, which are undesirable in shade and inferior in brilliance, are soluble under beater conditions, and possess an affinity for cellulose which is of a low order. The brightness of the direct dyes is amply sufficient in the great majority of fields of application provided the methods by which they are applied are such as are suitable.

COPPER TREATMENT

Although it is well known that the Sky Blues may be improved in fastness to light by a treatment with copper sulfate, it does not appear to be recognized widely that the treatment is of any decided practical value and may be extended to any considerable variety of dyes. The relative fastness of the copper lakes and the degree in which the fastness of the dye is effected by conversion into the lake, vary considerably with different dyes.

The influence of conversion into the lake upon the shade is equally variable. In general, the copper lakes are even duller than the aluminium lakes, but in numerous instances they are moderately bright and attractive in shade, while with certain direct yellows they are superior in desirability of shade to other metallic lakes of the dyes in question and but little duller than the latter. By the judicious employment of copper treatments in dyeing various individual dyes and dye combinations it is possible to obtain a great variety of shades of satisfactory brightness and excellent permanence.

The following dyes are improved in fastness in a material degree by conversion into the copper lakes:

Pontamine Sky Blue 5BX
 Pontamine Sky Blue 6BX
 Pontamine Blue AX
 Pontamine Copper Blue 2RX
 Pontamine Brown CG
 Pontamine Scarlet 4BS
 Pontamine Scarlet 8BS

With the exception of Pontamine Sky Blue 5BX, of which the lake is deficient in brightness, these dyes give lakes of satisfactory brightness and tinctorial power as well as of excellent fastness. The lake shade of Pontamine Blue AX is a neutral blue; that of Pontamine Sky Blue 6BX a very greenish blue, and that of Pontamine Copper Blue 2RX a very reddish blue, whereby a very extensive range of blue shades is possible.

A second list of dyes which are improved in fastness by copper sulfate in a degree which is moderate, although not sufficient to warrant the treatment in their cases, but which may be employed to advantage in shading the dyes of the first list, would include:

Pontamine Diazo Black BH Conc.
 Pontamine Blue BBF
 Pontamine Brown D3G
 Pontamine Fast Orange S

A third list of dyes which are not improved in fastness by a copper treatment but which retain their original excellent fastness and are only very slightly impaired in brightness thereby, and are, accordingly, also suitable for shading the dyes of the first list, would include:

Pontamine Brown R
 Pontamine Yellow CH
 Du Pont Brilliant Paper Yellow Conc.
 Pontamine Light Yellow 5GX

In the case of the last dye, the loss in brightness upon conversion into the lake is slightly greater than with the other dyes of the list but the fastness is excellent and the greenish cast of the shade thus obtained renders the dye particularly well adapted for employment with Pontamine Sky Blue 6BX in the production of fast greens.

Certain other direct dyes of excellent fastness, among which may be mentioned Pontamine Violet N, Pontamine Fast Pink BL, and Pontamine Fast Red F, give copper lakes which are of such inferior shades as to preclude the possibility of the employment of the dyes in conjunction with any copper treatment.

In the application of the copper treatment it is advisable to add the color to the beater first and to postpone the addition of the copper sulfate until after the color has been allowed to run for a short period, rather than to precede the addition of the color by that of the copper salt. The dyeings resulting from the former practice are somewhat stronger and brighter, as would be expected, and they are also distinctly faster to light. This may probably be explained upon the hypothesis that the lakes, although unquestionably materially faster than the corresponding dyes, are deposited entirely upon the fiber surface, in which position they are fully exposed to photochemical attack, whereas such portions of the color as have penetrated within the fiber substance are afforded some measure of protection from the influence of light through the absorption of active rays by the supernatant material and surface deposit of lake. With the possible exception of ground wood, it is advantageous to permit a measurable degree of absorption of dye before effecting the precipitation of the lake.

By the employment of the copper treatment with the dyes specified, it is possible to obtain a considerable range of attractive shades of excellent fastness which may hardly be duplicated by other means.

The Analysis of Beta-Naphthylamine¹

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This paper describes the analysis of β -naphthylamine, and includes methods by which pure β -naphthylamine and its common impurities, namely, β -naphthol, β,β -dinaphthylamine, and α -naphthylamine, were prepared, and some of their physical properties determined.

Methods for the determination of β -naphthylamine in the presence of these impurities are presented, together with tables showing the results obtained on a large number of technical and specially prepared laboratory samples. Special modifications of the Kjeldahl-Gunning Method have been developed which give theoretical results when applied to β -naphthylamine.

Specifications for technical β -naphthylamine are suggested. Melting-point curves are presented for the systems β -naphthylamine- β -naphthol; β -naphthylamine- β,β -dinaphthylamine; and β -naphthylamine- α -naphthylamine.

THE INCREASED use of β -naphthylamine in the manufacture of J-acid (2-amino-5-naphthol-7-sulfonic acid) and γ -acid (2-amino-8-naphthol-6-sulfonic acid) has emphasized the necessity for an accurate analytical method for its quantitative estimation in the presence of the more common impurities, namely, β -naphthol, β,β -dinaphthylamine and α -naphthylamine.

PRELIMINARY TREATMENT

PURIFICATION OF β -NAPHTHYLAMINE—Technical β -naphthylamine analyzing 98 per cent was dissolved in water as the hydrochloride, and the sulfate of the amine precipitated by the addition of sodium sulfate. The sulfate was filtered, placed in a separatory funnel, NaOH solution added, and the base extracted, as formed, with benzene. The base was precipitated from benzene as the hydrochloride with dry HCl gas, filtered, and the base prepared as before. The benzene solution was filtered, most of the solvent removed by direct distillation and the final traces by steam distillation. Distillation with steam was continued until approximately 50 per cent of the naphthylamine charged had been recovered. This was filtered, dried to constant weight over calcium chloride in vacuum, and ground to 80 mesh. The product was pure white in color, and odorless.

Melting point ² (corrected)	110.1° to 110.2° C.
Crystallizing point (corrected)	109.66° C.
Per cent nitrogen	Theory: 9.787; Found: 9.78, 9.75

(See Laboratory Sample 4, Table I.)

A second sample of β -naphthylamine was purified by repeated recrystallization from benzene. The same melting and crystallizing points were obtained as on the first sample. Liebermann and Jacobson³ give 111° to 112° C. or 112° to 113° C. as the correct melting point of β -naphthylamine. This point, frequently quoted in reference works, is undoubtedly too high.

PREPARATION OF β,β -DINAPHTHYLAMINE—The method of Merz and Weith⁴ using zinc chloride ammonia as a condensing agent was employed. The crude dinaphthylamine was extracted with hot benzene and crystallized out on cooling. After six recrystallizations from benzene the product came out as silvery leaflets having a slight yellow color and a decided fluorescence in benzene solution.

	THEORY	FOUND
Per cent nitrogen	5.20	5.18

¹ Presented before the Division of Dye Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² All melting points and crystallizing points recorded in this paper were taken with thermometers graduated in tenths of a degree and standardized by the U. S. Bureau of Standards.

³ *Ann.*, 211 (1882), 41.

⁴ *Ber.*, 14 (1881), 2343.

Liebermann and Jacobson³ give 170° C. and Palm⁵ records 170.5° C. as the correct melting point of β,β -dinaphthylamine. The melting point of the product from the 5th and 6th crystallizations was 172.2° C. (cor.).

PURIFICATION OF α -NAPHTHYLAMINE—Refined α -naphthylamine having a melting point of 46.5° C. and crystallizing point 45.65° C. (Dewar bulb) was recrystallized nine times from benzene. The crystals from the 7th, 8th, and 9th crystallizations, as well as the crystals obtained by evaporation of the mother liquors from the 8th and 9th crystallizations, all showed a melting point of 49.2° to 49.3° C. (cor.). The crystallizing point of this product, taken in a Dewar bulb, was 48.5° C. (cor.).

	THEORY	FOUND
Per cent nitrogen	9.787	9.76 9.77

The melting point recorded by Zinin,⁶ of 50° C., appears to be somewhat too high.

PURIFICATION OF β -NAPHTHOL—The β -naphthol used for the melting-point curve was a technical product which was twice recrystallized from water, had a melting point of 121.2° to 121.3° C. (cor.), and crystallized at 120.8° C. (cor.). Three samples of resublimed β -naphthol from different sources had the same melting and crystallizing points as mentioned above. Liebermann and Palm⁷ prepared β -naphthol from β -naphthylamine through the diazo reaction and obtained a melting point of 122° C. A repetition of their work gave a product with a corrected melting point of 120.65° C.

DIRECT NITRITE TITRATION METHOD

The results given in Table I, Method 1, were obtained using the same procedure as in Method 4, except that no separation of β -naphthol was made. A comparison of these results with those of Methods 2, 3, and 4 shows high analyses in proportion to the amount of β -naphthol present as an impurity. It is evident that this should be the case since, under the conditions of the analysis, nitroso- β -naphthol will also be formed. The direct titration of β -naphthylamine with 0.1 *N* sodium nitrite at 20° C. gives results higher than theory, even in the absence of β -naphthol, due apparently to the oxidation of diazo β -naphthylamine. Titration of technical samples with 0.5 *N* nitrite at 0° to 5° C. also yields results above theory, but which approach the true value more closely since oxidation is considerably checked at this temperature. In spite of these errors, many commercial laboratories and even manufacturers of β -naphthylamine still use this method with some slight modifications. The results obtained by this method are presented for comparative purposes in Table I, Method 1.

The attempt to devise a more accurate method of analysis resulted in the development of three methods, all applicable to technical materials, and each having certain advantages. The sulfonation method has the advantage of rapidity and simplicity, and is recommended where only the amine content is desired.

DETERMINATION OF β -NAPHTHYLAMINE

SULFONATION METHOD—Weigh 0.65 g. of the sample into a 50-cc. beaker, and add 20 cc. of 25 per cent oleum which has been previously cooled to 0° to 5° C. Stir with a glass rod and set the beaker in an ice bath. Stir occasionally and if necessary allow the sulfonation to come to room tempera-

⁵ *Ber.*, 15 (1882), 614.

⁶ *J. prakt. Chem.*, 27 (1883), 140.

⁷ *Ann.*, 183 (1876), 268.

ture to effect solution. Pour and wash the sulfonation into a 600-cc. beaker half filled with clean ice. Place the beaker on a tripod and bring to the boiling point. Boil gently for 15 min. to remove sulfur dioxide, and cool to 20° C. Bring the volume to 200 cc., add 15 cc. of concentrated hydrochloric acid, and titrate with 0.1 *N* sodium nitrite, using starch iodide as indicator. The titration proceeds rapidly to within a few tenths cc. of the end-point.

The end-point in the titration is reached if a distinct blue color develops 5 min. after the last addition of nitrite, when the solution is spotted against starch iodide solution on a spot plate.

1 cc. of 0.1 *N* nitrite = 2.202 per cent β -naphthylamine

0.5 *N* sodium nitrite and a 3.5-g. sample can also be used, but in this case the temperature should be lowered to 0° to 5° C. to avoid oxidation by the higher concentration of nitrous acid.

Sulfonation at low temperature results in the sulfonation of β -naphthol to β -naphthol-1-sulfonic acid, which does not absorb nitrite. The following results obtained with mixtures of β -naphthylamine and β -naphthol offer proof of this point:

MIXTURE	PER CENT β -NAPHTHYLAMINE FOUND	THEORY
I	82.47	82.46
II	81.47	81.75

Results of the analysis of seven technical and four laboratory samples by this method are presented in Table I, Method 2.

When the β -naphthylamine content and an accurate determination of the β -naphthol present are desired, the benzene separation method should be used.

BENZENE SEPARATION METHOD

DETERMINATION OF β -NAPHTHYLAMINE—Weigh 3.5 g. of the sample onto a watch glass, brush into a 500-cc. Erlenmeyer flask, add 300 cc. of dry benzene and dissolve. Insert a 2-hole rubber stopper, with calcium chloride drying tube, in one hole and in the other a $\frac{3}{16}$ -in. glass tube reaching to the bottom of the flask. Pass in HCl gas for 1 to 2 hrs., occasionally shaking the flask gently to insure thorough mixing and complete precipitation of the amine. Filter with suction through a 10-cm., double-jacketed, glass, hot-water funnel, using 2 filter papers and a platinum cone. Wash with 100 cc. of dry benzene saturated with HCl gas, and dry at 60° C. in vacuum. The precipitate adheres to the flask and necessitates drying the flask also, to obtain a complete recovery. Dissolve the hydrochloride in boiling water in a 600-cc. beaker, not allowing the volume to exceed 200 cc. Add 25 cc. of C. P. HCl, cool to 0° C., add a little ice to the solution, and titrate with 0.5 *N* sodium nitrite, as described under the sulfonation method.

1 cc. of 0.5 *N* sodium nitrite = 2.043 per cent β -naphthylamine

DETERMINATION OF β -NAPHTHOL—Evaporate the benzene filtrate to dryness on a steam bath, taking care to prevent the sublimation of β -naphthol when approaching dryness. Dissolve the β -naphthol with 10 cc. of 20 per cent caustic soda solution and dilute to 200 cc., heating, if necessary, to secure complete solution. Make slightly acid with HCl, add an excess of NaHCO₃ and couple with 0.05 *N* diazo *p*-nitrobenzene.

1 cc. of 0.05 *N* diazo *p*-nitrobenzene = 0.205 per cent β -naphthol

Results of the benzene separation are presented in Table I, Column 4.

Owing to the ease with which β -naphthylamine sublimes, together with the fact that certain naphthylamine mono-sulfonic acids are readily hydrolyzed back to the base, special

modifications of the Kjeldahl method were required to give quantitative results. Reference is made to the work of Green and Vakil⁸ for explanation of the type of sulfonation herein developed.

MODIFIED KJELDAHL-GUNNING METHOD

DETERMINATION OF TOTAL NITROGEN—Weigh 1.5 g. of the sample into a 50-cc. dry lipped beaker, add 20 cc. of 25 per cent oleum which has been previously cooled to 0° to 5° C. Stir with a glass rod, cover with a watch glass, and set the beaker in an ice bath. Stir occasionally, and, if necessary, allow the sulfonation to gradually approach room temperature to completely dissolve the larger crystals. Rinse down the sides of the beaker with 5 cc. of the oleum, cover with a watch glass, and let stand at room temperature (20° to 30° C.) for 15 hrs.

Transfer the sulfonation to an 800-cc., dry, Pyrex, Kjeldahl flask, through a long-stem, 2 $\frac{1}{2}$ -in. funnel. Wash the beaker with three 5-cc. portions of hot concentrated H₂SO₄, rinsing the funnel while transferring.

Add 1 g. of mercury and place a plug of glass wool $\frac{1}{2}$ to $\frac{3}{4}$ in. thick midway in the neck of the flask. Wet the plug uniformly, using 5 cc. concentrated H₂SO₄. Place the flask upon the digestion rack and apply the flame. Heat below the boiling point for 10 min., then more briskly until, after about 2 hrs., a nearly colorless solution is obtained. Wash down the neck of flask and glass wool with 5 cc. of hot concentrated H₂SO₄ and continue digestion for 10 min. While holding the flask in an inclined position, carefully push the glass wool into the flask with a glass rod. Add 8 to 10 g. of dry sodium sulfate and continue boiling for 1 to 2 hrs. after the solution has become colorless. Cool and dilute with 300 cc. of distilled water, rinsing down the neck of flask. Add 1 g. of pure granulated 20- to 30-mesh zinc, 40 cc. of sodium sulfide solution (containing 100 g. of crystalline or 50 g. of fused sodium sulfide per liter), and shake. Add 160 cc. 36° B_é. caustic soda solution, pouring it carefully down the side of the flask, connect immediately with the distillation apparatus and shake. (Pyrex-Davisson distilling bulbs were used.)

Distil into 50 cc. of standard 0.25 *N* HCl diluted with 50 cc. water, until 250 cc. have passed over. Titrate the remaining acid with standard 0.25 *N* sodium hydroxide, using methyl orange or congo red as indicator. In a similar manner make a blank determination on the reagents and correct for the amount of ammonia obtained.

1 cc. of 0.25 *N* HCl solution = 2.385 per cent β -naphthylamine

DETERMINATION OF ACID-INSOLUBLE MATTER

Weigh a 5-g. sample, dissolve in 150 cc. of boiling 1.5 per cent HCl, filter through a Gooch crucible which has been prepared with boiling water, wash with hot water, and dry at 100° C. to constant weight.

β -Naphthol, if present, will pass into the filtrate to the extent of at least 10 per cent. The insolubles include for the most part β,β -dinaphthylamine, being soluble under the conditions of the test to only 0.10 to 0.20 per cent. The β,β -dinaphthylamine can be isolated from the insoluble residue by solvent extraction, and either weighed or analyzed for nitrogen. The per cents of insolubles are given in Table I, Column 5.

DETERMINATION OF MELTING POINT

The melting points herein recorded for the pure compounds studied are at variance with those recorded in the literature. This is attributed, not so much to the greater purity of the compounds used (although great care was used in this work

⁸ *J. Chem. Soc.*, 113 (1918), 35; *C. A.*, 12 (1918), 804.

TABLE I

No.	METHOD OF ANALYSIS	TECHNICAL SAMPLES						LABORATORY SAMPLES				
		1	2	3	4	5	6	7	1	2	3	4
1	Titration with 0.5 N NaNO ₂ at 0° to 5° C., per cent.....	97.15	89.5	97.38	98.03	98.87	98.15	99.25	99.30	99.82
2	Sulfonation and titration with 0.1 N NaNO ₂ at 20° C., per cent.....	95.18 95.25	83.16	95.41	94.08	98.95 98.91	98.06	95.85	98.73	99.39	98.95	99.93 99.85
3	Kjeldahl-Gunning (modified) method, per cent	94.79	83.00	95.60	93.96	98.42	98.15 97.71	96.27	98.70	99.01	99.20	99.89 99.58
	Benzene separation, per cent amine.....	95.37	83.16	95.59	94.27	98.79	97.88	98.79	99.08	99.19	99.82
	Per cent naphthol....	3.10	8.49	2.99	4.37	0.12	0.20	0.04	0.22	None	None
5	Insoluble, per cent.....	0.23	2.04	0.23	0.24	0.21	0.32	0.12	None	None	None
6	Melting point (° C.)....	109.5	108.1	109.4	109.4	110.0	109.8	109.3	110.0	110.0	110.1	110.1 110.2

to obtain pure products), as to the fact that more accurately standardized and more finely graduated thermometers were available. Care was taken in making the observations to obtain a uniform temperature rise of 0.1° C. every 15 sec. during the last degree rise. The usual correction for stem exposure, which apparently was never used in the earlier work, was applied in all cases.

Capillary tubes of about 0.5-mm. internal diameter were made from glass tubing, which was previously cleaned with chromic acid solution, washed with distilled water, and dried with hot air.

For the melting-point determination, a portion of the finely ground sample was dried over sulfuric acid *in vacuo*, placed in a capillary tube, and attached to the thermometer which was immersed in a colorless oil bath in the usual manner.

The melting points, or minimum temperature of complete liquefaction, appear in Table I, Column 6.

MELTING-POINT CURVES—The pure compounds previously described were used in the preparation of the melting-point curves (Fig. 1) of the binary systems β -naphthylamine- β -naphthol, β -naphthylamine- β,β -dinaphthylamine, and β -naphthylamine- α -naphthylamine.

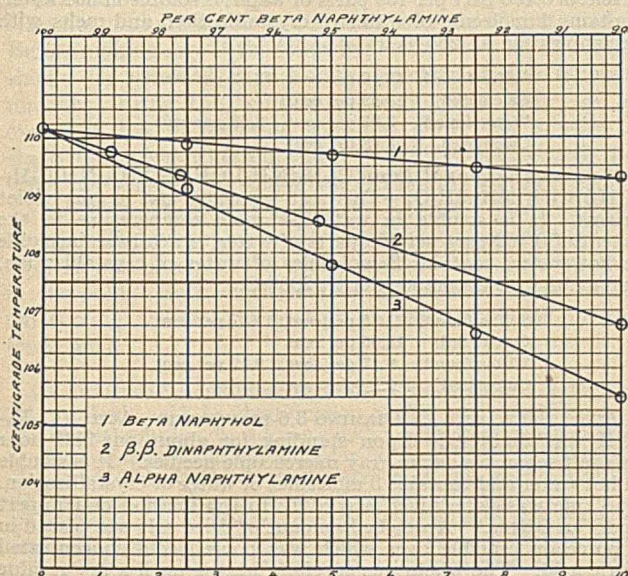


FIG. 1

The mixtures containing the desired weights of material were placed in a Parr sulfur bomb, which was tightly closed, and heated in an air oven for 15 min. at a temperature 5° to 10° above the melting point. The solid mass was removed as completely as possible, finely ground in an agate mortar, and the melting point determined.

Reference is made to the work of Kremann and Strohschneider⁹ presenting the complete crystallizing-point curve for the system β -naphthylamine- β -naphthol. Their crystallizing points of 48.0° C. and 109.0° C. for α - and β -naphthylamine, respectively, are in fair agreement with those determined in this work. Their crystallizing point of 122° C. for β -naphthol is, however, undoubtedly too high.

DETERMINATION OF MOISTURE

Moisture determinations were not made on the entire series of samples because in many cases these were exhausted. However, even those which were not dried to constant weight in their preparation for analysis contained but very little moisture.

The moisture determination is made by drying a finely powdered 5-g. sample to constant weight over concentrated sulfuric acid *in vacuo*.

A sample of dry β -naphthylamine under these conditions remained constant in weight over a period of 4 days.

DISCUSSION OF METHODS AND RESULTS

In practice, the β -naphthylamine content is estimated by the sulfonation method and the melting point determined. If the amine content is 96 per cent or higher and the melting point is 109° C. or higher, the absence of any appreciable amount of impurities is assured.

If the material does not meet these specifications, the impurities are investigated further by determining the β -naphthol content by the benzene separation method and the β,β -dinaphthylamine by the solubility test.

In the benzene separation, β,β -dinaphthylamine passes into the filtrate, even to the extent of 20 per cent of the sample specified.

In the absence of appreciable amounts of β -naphthol or dinaphthylamine, the melting point of the product when compared with Fig. 1, Curve 3, offers an indication of the amount of α -naphthylamine present.

SPECIFICATIONS

In order to assist in the standardization of technical β -naphthylamine, the following specifications are suggested:

Melting point.....	Not less than 109.0° C. (cor.)
β -Naphthylamine.....	Not less than 98.0 per cent
β -Naphthol.....	Not more than 3.0 per cent
Insolubles.....	Not more than 0.5 per cent
Moisture.....	Not more than 0.5 per cent

⁹ *Monatsh.*, 39 (1918), 505; *C. A.*, 13 (1919), 2475.

Civil Service Examinations

The United States Civil Service Commission has announced examinations for junior engineer, junior physicist, and junior technologist, on November 22, 1922, to fill vacancies in the Bureau of Standards, Washington, D. C., or elsewhere, at \$1200 to \$1500 a year.

Substituted Naphthalene-sulfonic Acids^{1,2}

I—A Method for Identifying H-Acid and Its Intermediates Obtained from Naphthalene-2,7-disulfonic Acid

By D. F. J. Lynch

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A method is here proposed for detecting 1,8-dinitro-3,6-naphthalenedisulfonic, 1,8-diamino-3,6-naphthalenedisulfonic, 1,8-amino-naphthol-3,6-disulfonic (H-acid), and 1,8-dihydroxy-naphthalene-3,6-disulfonic (chromotropic) acids, which occur in the nitration of naphthalene, 2,7-disulfonic acid and the subsequent reduction and hydrolysis of the dinitro acid.

THE POSSIBILITY of detecting and identifying H-acid and its intermediates by means of their insoluble organic salts was suggested by Ambler's³ work on the naphthalenesulfonic acids. In the work here reported a large number of organic salts were prepared, but only the more insoluble ones were further studied. The method of making the salts was the same in each case. Molecular equivalent quantities of an inorganic salt of the acid and the hydrochloride of the organic base were dissolved separately in water at room temperature, the two solutions mixed, stirred thoroughly, and allowed to stand for about one-half hour. The crystallized salts were filtered, washed with cold water, and dried in the air.

All the salts were analyzed for water of crystallization in the following manner: From 2 to 3 g. of each salt, after being dried in the air, were allowed to stand in a large closed compartment until a constant weight was reached; then the salt was dried at 100° C. over sulfuric acid in a vacuum oven; the weighing bottle containing the salt was closed, put in a desiccator, allowed to cool, and weighed.

The sulfur in these salts was determined by ignition with sodium peroxide, as described by Ambler.⁴

ANALYSIS OF SALTS

BENZIDINE SALT OF 1,8-DINITRO-NAPHTHALENE-3,6-DISULFONIC ACID (C₁₀H₄(NO₂)₂(SO₃H)₂.NH₂C₆H₄.C₆H₄NH₂)—This salt separates out in light yellow prisms. At 20° C., 0.036 part of this salt dissolves in 100 parts of water to give a colorless solution. It is almost equally insoluble in hot water. It contains no water of crystallization and melts with decomposition at 275° C.

Sulfur found, 11.58 per cent, 11.25 per cent
Calculated, 11.39 per cent

CYMIDINE-1,8-DINITRO-NAPHTHALENE-3,6-DISULFONATE (C₁₀H₄(NO₂)₂(SO₃H)₂.[NH₂C₆H₃(CH₃)CH(CH₃)₂]₂)—This salt separates out in straw-colored prisms. It is soluble in water at room temperature to the extent of 0.059 part in 100 parts of water. It is soluble in hot water, contains no water of crystallization, and melts with decomposition at 265° C.

Sulfur found, 9.53 per cent, 9.64 per cent
Calculated, 9.47 per cent

BENZIDINE SALT OF CHROMOTROPIC ACID (C₁₀H₄(OH)₂(SO₃H)₂.NH₂C₆H₃(CH₃)CH(CH₃)₂)—This salt separates out in brown prisms. It is soluble at room temperature in water to the extent of 0.085 part per 100 parts of water. It is nearly as insoluble in hot water, contains no water of crystallization, and melts with decomposition at 278° C.

¹ Received December 2, 1921.

² Contribution No. 57 from the Color Laboratory, U. S. Bureau of Chemistry, Washington, D. C. Published with permission of the Department of Agriculture.

³ "Naphthalene Sulfonic Acids. II—A Method for the Qualitative Detection of Some of the Naphthalene Sulfonic Acids," by J. A. Ambler and E. T. Wherry, THIS JOURNAL, 12 (1920), 1085.

⁴ THIS JOURNAL, 12 (1920), 1081.

Sulfur found, 12.89 per cent, 12.81 per cent
Calculated, 12.70 per cent

p-NITROTOLUIDINE-1,8-DIAMINO-NAPHTHALENE-3,6-DISULFONATE (C₁₀H₄(NH₂)₂(SO₃H)₂.[NH₂C₆H₃(NO₂)CH₃]₂)—This salt separates out in grayish tan needles. It is soluble in water at room temperature to the extent of 0.186 part per 100 parts of water. It is soluble in hot water, contains no water of crystallization, and melts with decomposition at 270° C.

Sulfur found, 10.15 per cent, 10.35 per cent
Calculated, 10.29 per cent

m-α-NAPHTHYLAMINE SALT OF H-ACID (C₁₀H₄(NH₂)(OH)(SO₃H)₂.NH₂C₁₀H₇)—This salt separates out in light violet-gray prisms, is soluble in water at room temperature to the extent of 0.1006 part per 100 parts of water and nearly as insoluble in hot water, contains no water of crystallization, and melts with decomposition at 278° C.

Sulfur found, 13.67 per cent, 13.71 per cent
Calculated, 13.85 per cent

m-PSEUDOCUMIDINE SALT OF H-ACID (C₁₀H₄(NH₂)(OH)(SO₃H)₂.NH₂C₆H₃(CH₃)₃)—This salt separates out in gray prisms. It is soluble in water at room temperature to the extent of 0.097 part per 100 parts of water, is nearly as insoluble in hot water, contains no water of crystallization, and melts with decomposition at 272° C.

Sulfur found, 13.93 per cent, 13.98 per cent
Calculated, 14.10 per cent

m,p-NITROTOLUIDINE SALT OF H-ACID (C₁₀H₄(NH₂)(OH)(SO₃H)₂.NH₂C₆H₃(NO₂)(CH₃).H₂O)—This salt separates out in gray prisms. It is soluble in water at room temperature to the extent of 0.106 part per 100 parts of water, is soluble in hot water, contains 1 molecule of water of crystallization, and melts with decomposition at 265° C.

Sulfur found, 13.40 per cent, 13.51 per cent
Calculated, 13.59 per cent
Water found, 3.62 per cent, 3.58 per cent
Calculated, 3.68 per cent

TOLIDINE SALT OF H-ACID (C₁₀H₄(NH₂)(OH)(SO₃H)₂.NH₂C₆H₃(CH₃)(C₆H₅)NH₂.3H₂O)—This salt separates out in gray-violet prisms. It is soluble in water at room temperature to the extent of 0.102 part per 100 parts of water, is nearly as insoluble in hot water, contains 3 molecules of water of crystallization, and melts with decomposition at 260° C.

Sulfur found, 11.95 per cent, 11.87 per cent
Calculated, 12.05 per cent
Water found, 9.17 per cent, 9.12 per cent
Calculated, 9.23 per cent

ZINC SALT OF 1,8-DIAMINO-3,6-DISULFONIC ACID (C₁₀H₄(NH₂)₂S₂O₆Zn.3H₂O)—Upon standing for about one-half hour this salt separates out in gray microscopic needles. It is soluble in hot water and contains 3 molecules of water of crystallization. The zinc was determined according to the method of Huppert and Van Ritter.⁵ A weighed amount of dried salt was placed in a porcelain crucible over which was poured cold concentrated nitric acid. The whole was carefully heated until a dry residue remained, then ignited until the residue while hot was pure white. This salt dissolves to the extent of 6.4 parts per 100 parts of water at 20° C. The excess of zinc sulfate reagent has a salting-out effect.

Zinc found, 17.25 per cent, 17.18 per cent
Calculated, 17.06 per cent
Water found, 12.40 per cent, 12.49 per cent
Calculated, 12.47 per cent

⁵ Z. anal. Chem., 35 (1896), 311.

IDENTIFICATION OF H-ACID AND INTERMEDIATES

(Tests are to be made in 5 to 10 per cent hydrochloric acid solutions, except those with cobalt chloride and zinc sulfate, which are made in neutral solutions)

	Benzidine-HCl	2-Cymidine- H ₂ SO ₄ (CH ₃ =1)	α -Naphthyl- amine-HCl	Pseudocumi- dine-HCl	Tolidine-HCl	<i>p</i> -Nitrotolu- idine-HCl (1-2-4)	CoCl ₂	ZnSO ₄
1,8 - Di - No- 3,6-disulfonic acid of naph- thalene	Immediate ppt. Light straw- yellow. Wait 5 min.	Immediate light straw- yellow ppt. Wait 10 min.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
1,8 - Di - NH ₂ - 3,6-disulfonic acid of naph- thalene	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	Gray-tan ppt. Let stand 15 min.	Brown ppt. Let stand 1/2 hr.	Ppt. brown. Let stand 1/2 hr.
1 - NH ₂ - 8- OH - 3,6 - di- sulfonic acid of naphtha- lene (H-acid)	A ppt. is formed on long stand- ing from a conc. solu- tion	No ppt.	Ppt. light violet - gray. Let stand 15 min.	Ppt. tan-gray. Let stand 10 min.	Ppt. gray- violet. Let stand 10 min.	Ppt. gray. Let stand 10 min.	No ppt.	No ppt.
1,8 - Di - OH- 3,6-disulfonic acid of naph- thalene (chromo- trophe acid)	Immediate brown ppt. Wait 10 min.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.

COBALT SALT OF 1,8-DIAMINO-3,6-DISULFONIC ACID (C₁₀H₄(NH₂)₂S₂O₆Co.2H₂O)—Upon standing for one-half hour this salt separates out in brown microscopic needles. It is soluble in hot water and contains 2 molecules of water of crystallization. The cobalt was determined by heating the cobalt salt slowly and carefully and then igniting the residue of cobalt oxide. This salt dissolves at 20° C. to the extent of 6 parts per 100 parts of water. Here again the excess of the molar solution of cobalt chloride has a salting-out effect on the salt.

Cobalt found,	15.31 per cent,	15.37 per cent
Calculated,	15.51 per cent	
Water found,	8.71 per cent,	8.68 per cent
Calculated,	8.80 per cent	

METHOD OF IDENTIFICATION

All the tests may be made in test tubes with 3 to 5 cc. of dilute solutions—for example, of concentration less than tenth molar. The organic reagents should be prepared upon the same day as needed by dissolving the organic base in a 10 per cent solution of hydrochloric acid. The zinc and cobalt reagents used are molar solutions of the salts of these metals. Before making any of the following tests, however, all sulfates should be removed with barium chloride in the following manner: Bring the solution to boiling and then add an excess of barium chloride solution; allow the solution to stand on the water bath until the precipitate has settled, then filter and wash; bring the filtrate to boiling and add sodium carbonate solution to remove the barium. Neutralize the filtrate with hydrochloric acid. Of the four acids studied only two, H- and chromotrope acids, form barium salts insoluble in the cold. Both of these salts are soluble in hot water. On cooling, therefore, a precipitate indicates H- or chromotrope acid.

1,8-DIAMINO-3,6-DISULFONIC ACID—First test for 1,8-diamino-3,6-disulfonic acid, as identification of this acid should be made in a neutral solution, by adding a molar solution of cobalt chloride or zinc sulfate. After standing for one-half hour, the formation of a precipitate indicates the presence of this acid. The precipitate is compact and slow in forming. The presence of the other three acids, however, does not interfere with this precipitation. If, later on, no H-acid is found, 1,8-diamino-3,6-disulfonic acid can be quickly identified and confirmed with the reagent *p*-nitrotoluidine (1,2,4) hydrochloride. This reagent gives an immediate grayish tan precipitate with the diamino acid.

The tests for the other three acids are made in acid solution. Add enough hydrochloric acid to make the resulting mixture a 5 per cent acid solution and let stand one-half hour. If the solution so treated is a concentrated solution of H-acid, its acid sodium salt will be precipitated. Filter out this acid salt. The amount of H-acid left in solution can be easily detected with any of the reagents given in the table and the

resulting dilute solution of H-acid will not interfere with the tests for the other acids.

1,8-DINITRO-3,6-DISULFONIC ACID—As seen from the table, cymidine hydrochloride will precipitate only this acid from any mixture of acids of this group. This test should be made before the removal of H-acid, when such removal is necessary, as this acid, like many other nitro compounds, decomposes upon heating. If, however, no chromotrope or H-acid is found afterwards, benzidine hydrochloride will serve as a reagent in confirming the presence of the dinitro acid. There is no difficulty in distinguishing the benzidine salt of the dinitro acid from the one formed with chromotropic acid. These two acids almost never occur in the same working mixture. With such a mixture, however, all the dinitro acid should be removed with a large excess of cymidine hydrochloride. Filter out the dinitro salt and neutralize the filtrate with sodium hydroxide. Filter the free base and evaporate the filtrate down to the original volume before testing for chromotropic acid.

1,8-AMINONAPHTHOL-3,6-DISULFONIC ACID (H-ACID)—This acid is identified by the formation of an insoluble salt with α -naphthylamine, tolidine or pseudocumidine hydrochloride in a 5 to 10 per cent acid solution. These reagents do not form insoluble salts with the other three acids. *p*-Nitrotoluidine hydrochloride also forms an insoluble salt with H-acid in an acid solution, which will serve for identifying the acid if no diamino acid is present.

Definite positive tests have been obtained in the Color Laboratory with 2 cc. of 0.01 *M* solution of H-acid upon the addition of 2 cc. of 0.1 *M* solution of tolidine hydrochloride or *p*-nitrotoluidine hydrochloride. The results of these tests show that by this method it is possible to detect as small amounts as 0.3 per cent of H-acid in a 5 per cent solution of hydrochloric acid. *p*-Nitro-*o*-toluidine hydrochloride and pseudocumidine hydrochloride are better reagents because the salts formed are flocculent. In dilute solution the precipitates form more slowly and at least one-half hour should be allowed for the tests.

Before testing for chromotropic acid remove the H-acid present in the following manner: Add an excess of *p*-nitrotoluidine reagent and allow solution to stand one-half hour for complete precipitation. Filter, and neutralize with sodium hydroxide solution. Filter out the free base and evaporate the solution to its original volume. The solution can then be tested for chromotropic acid.

1,8-DIHYDROXY-3,6-DISULFONIC ACID—If H-acid was present and removed with *p*-nitrotoluidine hydrochloride, test again with that reagent to make sure of the complete removal of H-acid, after which identify chromotropic acid with benzidine hydrochloride.

Experiments with Florida clay deposits, made possible by the cooperation of various Florida cities, are now being conducted at Cornell University to determine whether these clays can be used for the manufacture of brick, tile, and pottery. Clays suitable for filler are also being tested.

Coke Residue Test for Creosote Oils¹

By Charles S. Reeve and Frank W. Yeager

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DURING the past year the authors' attention was called to rather marked discrepancies in the results of this test,² not only in different laboratories but with the same operator when testing oils especially prepared and distributed for comparative work.

The possible variations in the test were first shown by experiments on two samples of oils distributed to four laboratories with instructions to follow the method outlined. The results of these experiments are given in Table I.

TABLE I

Test	SAMPLE 1				SAMPLE 2			
	A	B	C	D	A	B	C	D
1	8.0	10.8	9.2	11.8	4.2	7.6	6.3	7.3
2	7.3	11.1	10.5	12.3	4.0	7.2	6.1	7.8
3	8.00	7.8	10.3	10.1	4.1	6.8	6.4	7.3
4	8.0	9.2	9.9	9.9	4.4	...	5.8	7.3
5	9.9	...	4.2	...	5.2	...
6	4.4
Av.	7.8	9.7	10.0	11.0	4.2	7.2	6.0	7.4

These results show a remarkable dissimilarity between the different laboratories on the same oils, and a general failure to get close checks even in the same laboratory. The variations of the tests in the individual laboratories expressed as maximum per cent variation from the average are:

LABORATORY	Sample 1 Per cent	Sample 2 Per cent
A	9	5
B	20	6
C	8	13
D	12	5

The variation between laboratories on the same oil is 19 per cent for Sample 1, and 32 per cent for Sample 2. Inasmuch as this test is used as a basis for estimating the amount of refined tar blended in a finished creosote, and as the oils are often required to fall within a specified limit in this respect, it is readily seen from these results that the test is not satisfactory.

¹ Received May 4, 1922.

² Am. Soc. Testing Materials, Standard D-38-18.

This wide variation in results led to a consideration of the factors that might be responsible. Our conclusions may be summarized as follows:

(1) **SHAPE OF BULB**—While the specifications for a bulb are narrow as to shape and dimensions, we have found it practically impossible to obtain the desired uniformity, and it is usually necessary to select from a large lot those which most closely approximate the specification.

(2) **CHARACTER OF GLASS**—Many of the bulbs on the market are made of a soft glass, which either prevents the proper application of the full flame heat, or through fusion and consequent shrinkage of the glass walls causes a change in the relation of volume of oil to bulb capacity.

(3) **RATE OF DISTILLATION**—It is difficult to keep this constant on account of the small vapor space above the oil and because of the frequent necessity of conducting the distillation intermittently in order to avoid spurting, particularly when the oil contains traces of water.

Efforts were made to minimize these effects by purchasing a few special hard-glass bulbs that came very near the specifications, but in no case was there any material increase in the ability to obtain better check results. These results are included in Table II. This investigation led to the conclusion that some method should be devised that would eliminate coking in glass, but at the same time give results more nearly constant and substantially in accord with those heretofore obtained in the bulb, and so avoid as far as possible any conflict with existing oil specifications. This involved a distillation with subsequent coking of the residue and it was decided to associate the coke test with the retort distillation as given in American Society Testing Materials D-38-18.

The following procedure was therefore devised: (1) The oil was subjected to retort distillation; (2) the residue above 355° C. was subjected to the test for fixed carbon (A. S. T. M. D-22-16) using a Bunsen burner; (3) the percentage of fixed carbon (coke) was calculated back to the original sample of oil. In trying out the method, each of four oil samples was tested by two operators. Table III gives the distillation tests, percentage of coke on residue, and calculated percentage of coke on the oil.

TABLE II—SUMMARY OF TESTS COMPARING COKE-BULB AND RESIDUE-CRUCIBLE TESTS OF CREOSOTE OIL COKE

Sample of oil	3 ¹		4 ²		5 ¹		6 ²	
	1	2	1	2	1	2	1	2
Operator								
Coke-bulb tests, per cent variation	..	9.4	..	5.7	3.2	3.7	0.9	..
Retort distillation, per cent distillate:		±10.	..	±10.	±10.	±10.	±27.	..
0-170° C.	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
0-210	3.3	3.0	3.2	4.7	0.4	0.2	0.5	0.4
0-235	27.6	26.2	32.2	34.6	4.6	2.4	1.8	2.3
0-270	48.0	48.6	56.0	57.3	22.0	20.1	15.3	16.4
0-315	59.6	60.1	68.2	69.4	42.5	42.3	42.0	40.9
0-355	70.3	70.5	78.6	79.5	70.7	69.1	73.6	73.9
Residue	29.0	28.9	20.2	20.4	28.7	30.7	25.3	25.7
Loss	0.7	0.6	1.2	0.1	0.6	0.2	1.1	0.4
Residue-Crucible Test	I	II	I	II	I	II	I	II
	28.1	8.1	27.8	8.0	25.9	5.2	25.0	5.1
	27.5	8.0	27.8	8.0	25.9	5.2	25.3	5.2
	27.8	8.1	28.0	8.1	25.8	5.2	25.3	5.2
	28.0	8.1	..	25.8	5.2
Av. per cent coke in oil	8.1	..	8.0	..	5.2	..	5.2	..
Per cent variation	±1.	..	±1.	..	0.	..	±2.	..
Type of crucible	(a)	..	(a)	..	(a)	..	(b)	..
Range of per cent coke by bulb test	8.5 to 10.2		5.4 to 6.3		2.9 to 3.6		0.7 to 1.0	
Per cent coke by special hard bulbs	..		5.0-6.2		
	..		Av. 5.6		

I—Per cent fixed carbon in residue.
II—Per cent coke, whole oil basis.

¹ Refined tar solutions.
² Distillate oil.

a—10 cc. capsule type of crucible.
b—20 cc. regular form of crucible.

TABLE III

Operator	Residue: 20-cc. Platinum Crucible			
	Sample 3		Sample 4	
	1	2	1	2
Per cent coke	8.1	7.9	5.2	5.2
Average	8.0		5.2	

In the residue-crucible test the variation in the results of the same operator, or between two operators, is practically negligible. Furthermore, the results of the tests are comparable with the average of the regular coke-bulb test.

A few other trials were made on Oil Samples 3 and 4 using the regular type 20-cc. in place of the 10-cc. capsule crucible. These results are practically the same as those obtained by the 10-cc. platinum crucible (Table II).

To determine the possibility of further simplifying the test, some coke determinations using the crucible method and charging the oils direct to the crucibles without previous distillation, were made.

TABLE IV

Crucible	Oil Charged Direct to Crucible			
	Sample 3		Sample 4	
	10 cc.	20 cc.	10 cc.	20 cc.
Per cent coke	6.20	7.03	3.06	4.70
Per cent coke	6.38	6.31	3.28	4.66
Average	6.3	6.7	3.2	4.7
Range of per cent coke by bulb test	8.5 to 10.2		5.4 to 6.3	

This last procedure was not considered satisfactory with either crucible, mainly on account of the failure of the results to approximate a regular bulb test.

Reference to the tabulation will show that residue-crucible results are always slightly lower than the average coke-bulb results.

Oil sample	3	4	5	6
Per cent coke (bulb method)	9.6	5.7	3.2	0.9
Per cent coke (residue-crucible method)	8.1	5.2	2.8	0.7
Range of bulb tests	8.5 to 10.2	5.4 to 6.3	2.9 to 3.6	0.65 to 1.0

This condition may be due to the softness of the glass bulbs which, as previously noted, makes it impossible to apply the full flame heat for period adequate for igniting the residue. Such limiting of ignition results in leaving a residue that is not entirely coked and consequently of greater per cent than an equivalent completely coked residue. Under such conditions the degree of coking may in some instances be carried further than in others, and these tests would represent purer coke residues, which, other things being equal, are indicated by the lowest per cent of coke. It is apparent on comparing the lowest bulb results with the residue-crucible averages that this assumption is approximately correct. This is also evidenced by the tests on Sample 4 using the special very hard glass bulbs, where the coke obtained by the residue-crucible method falls within the limits of the bulb variations,—i. e., the range of bulb test is 5.0 to 6.2 per cent, and the average of residue-crucible tests is 5.2 per cent.

TABLE V—COMPARISON OF BULB AND CRUCIBLE TESTS BY DIFFERENT LABORATORIES

Oil sample	7			8			9		
	A	B	C	A	B	C	A	B	C
Per cent coke by bulb	8.9	8.2	8.2	5.1	4.7	5.4	6.5	5.9	7.1
Variation	..	±6.	±8.	±9.	..
Average of bulb test	..	8.4	5.0	6.5	..
By residue-crucible	7.7	8.0	8.1	4.4	4.2	4.6	5.3	5.4	5.3
Variation	..	±2.5	±4.6	±1.9	..
Average residue-crucible tests	..	7.9	4.4	5.3	..
Difference between methods	..	0.5	0.6	1.2	..
Sp. gr. of oil	..	1.093	1.087	1.118	..
Per cent residue to 355° C.	..	28.3	22.5	39.4	..

Thus it appears that the residue-crucible method, while yielding results somewhat lower than the usual bulb tests, indicates more truly the actual coke content of the oil, and that as the hardness of the bulbs is increased the results by the two methods become more nearly equivalent.

A recent trial of the crucible method on three oils by different laboratories gave the results in Table V.

CONCLUSIONS

It has been found that the percentage of coke in an oil as determined by the coke-bulb test is subject to variations over undesirably wide limits, owing to unavoidable variations in test conditions, and that a crucible test wherein the percentage of coke is calculated from a fixed carbon test on the residue of the oil remaining after a retort distillation to 355° C. has the following points to recommend it as a substitute for the bulb test:

- 1—The results are sufficiently close to the average of a number of regular coke tests to offer comparable values.
- 2—The accuracy of the method is greater than that of the present coke-bulb test.
- 3—The procedure itself is very simple, and requires no apparatus that is not usually found in laboratories where general tar and oil tests are made.
- 4—The difficulty and expense of obtaining truly satisfactory coke bulbs are eliminated.
- 5—The oils are usually given retort distillation tests and the residue can be used for the coke test. The total time per test in such cases is, therefore, only about 15 min.

Priestley Apparatus at Dickinson College, Carlisle, Pa.

Dickinson College has for over a century treasured some fine pieces of apparatus once owned by Joseph Priestley. They were purchased for the sum of \$530 by Thomas Cooper, who in 1811-1815 was professor of chemistry and mineralogy at Dickinson.

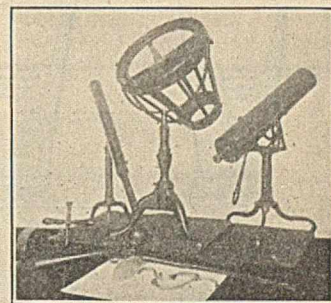
The burning glass is composed of two lenses, 16 and 7 in. in diameter, and set 16 in. apart. The wooden frame permits adjustment to suit the altitude of the sun.

The reflecting telescope is of the Gregorian type. The main mirror is 5 in. in diameter, and is mounted in a brass tube 2.5 ft. long. The maker was W. S. Jones, London.

The achromatic refracting telescope is 4 ft. long. It was made by Dolland.

The air gun was probably designed by Priestley himself. The air magazine is a wrought iron globe, 3.5 in. in diameter.

There are also flasks with ground necks and tubes with ground stoppers.



Another Platinum Theft

The following platinum articles were stolen from Vanderbilt University, Nashville, Tenn., between August 1 and 8, 1922:

	Approx. Weight Grams
Crucibles	
No. 3, with lid	19.1
No. 9, with lid	28
No. 14, with lid	39.8
No. 30, with lid	22.8
No. 34, with lid	27.5
No. 44, without lid	4.6
Milk Dish	
No. 9, gold	16.1
Combustion Boats	
No. 4, No. 5	7.1, 15.2
Dishes	
No. 20, No. 21	40.3, 31.2
Platinum combustion tube, complete, unused (E. & A. No. 5402)	377

The university will greatly appreciate any information leading to the recovery of any of these articles.

The Technical Chemistry of Vanadium¹

By B. D. Saklatwalla²

VANADIUM CORPORATION OF AMERICA, BRIDGEVILLE, PENNSYLVANIA

THE ELEMENT vanadium was discovered about a hundred and twenty years ago in 1801 in the lead ores of Mexico by Manuel del Rio. Thirty years later Berzelius had studied and worked out the chemistry of this element. By the year 1870 Roscoe had supplemented Berzelius's work and practically exhausted the study from a chemical standpoint.

In spite of this early work, vanadium had not entered the sphere of commercial technology until within the last very few years. In the sixties there was some demand for vanadium in the dyeing industry, in the preparation of aniline black. It was also used in the manufacture of inks, and for coloring glass and pottery, brown, purple, blue, and green glazes being prepared with it. Its salts had also been suggested as photographic developers, and as catalyzers in the contact process of sulfuric acid manufacture. Also its compounds had been tried as therapeutic agents owing to their strong oxygenating properties, and they had also been recommended as antiseptics. Further, their use was tried in the laboratory, as a reagent for alkaloids and hydrogen peroxide, and for the determination of hydrazine and hydroxylamine in the presence of ammonia.

The technical use of vanadium on a commercial scale, however, began when it entered the metallurgical field. In 1894 Moissan experimented on the reduction of vanadium in the electric furnace. In 1896 the Firminy Steel Works in France experi-

mented with its use in armor plates. In 1900, however, Professor Arnold in Sheffield, England, undertook a comprehensive study of its effects in steel, and that date may be considered as its real entry into the commercial metallurgical field.

The reason for a century-long neglect of this element is to be found mainly in the fact that until comparatively recently no commercially workable deposits of vanadium minerals were known. The vanadium was extracted from slags, ashes of vanadium-bearing coals, and the like. The processes employed were long and wasteful, and consequently the cost of the vanadium was prohibitively high. Fortunately about the time its usefulness was proved in steel metallurgy by Professor Arnold, the largest known deposits of vanadium in the Peruvian Andes were discovered, consisting of the mineral patronite, a vanadium sulfide. Subsequently, in this country, deposits of vanadiferous sandstone and carnotite have been worked. The vanadiferous sandstone contains as one of its constituents "Roscolite," a vanadiferous mica. The carnotite carries its vanadium in combination with uranium. With the discovery of these deposits the metallurgical application of vanadium advanced rapidly.

CHEMICAL REACTIVITY OF VANADIUM

From the chemists' standpoint the element vanadium presents very interesting features which can scarcely be found in any other element. It possesses a reaction capability enabling it to form an extensive number of different compounds. We

¹ Presented before the New York Section of the American Chemical Society, New York, N. Y., June 9, 1922.

² General Superintendent, Vanadium Corporation of America.

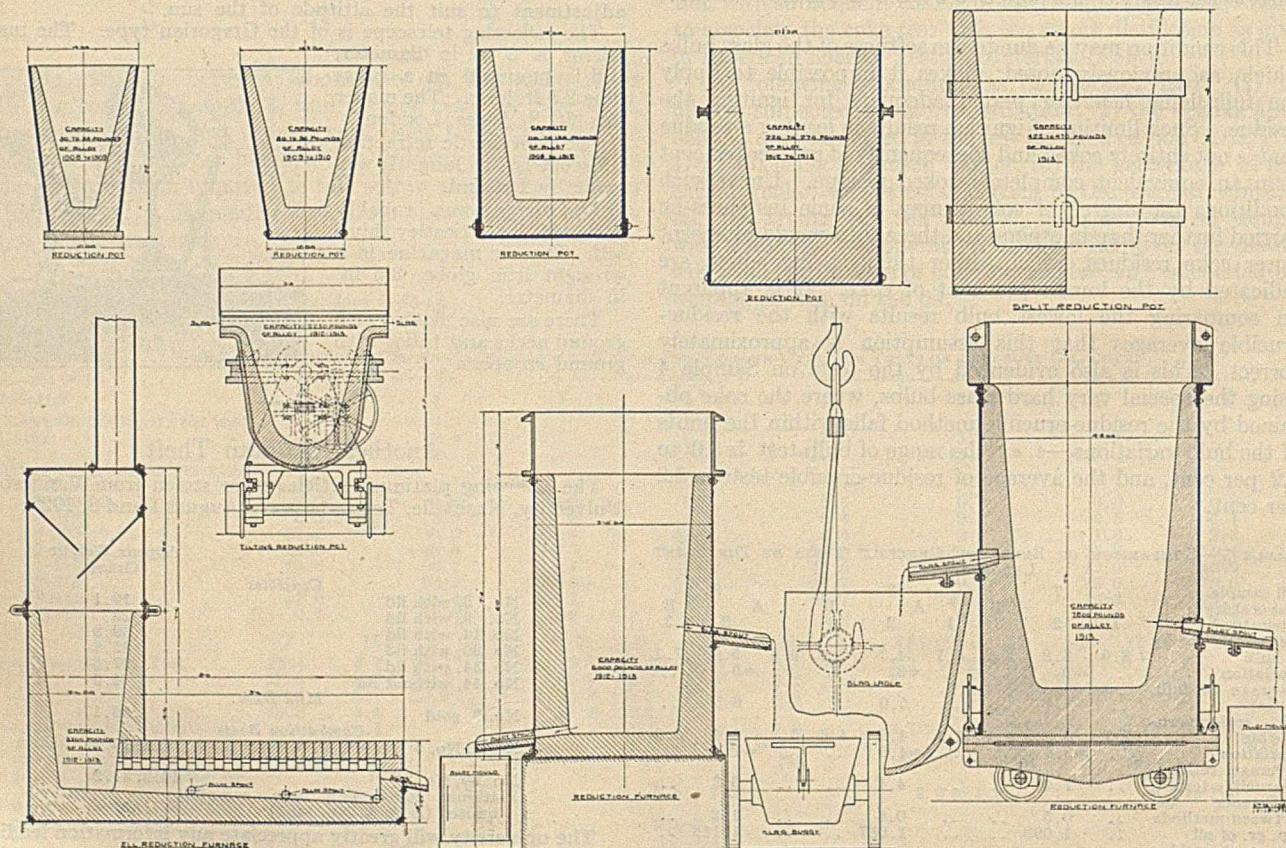


FIG. 1

can readily understand this capability when we consider its position in the periodic system. It stands in the fifth group of elements vertically with N, P, As, Sb, and Bi, between P and As, and horizontally its atomic weight places it between Ti and Cr. Consequently, it shares the property of this group of functioning in different valencies and forming basic as well as acid radicals. Combined with this, its proximity to chromium imparts to it the capability of forming double salts.

The element vanadium occurs in its compounds in the di-, tri-, tetra-, penta-, and hexavalent states. The salts corresponding to the lowest oxide, VO or V_2O_3 , are powerful reducing agents, capable of bleaching organic coloring matter and reducing copper, tin, silver, gold, platinum, and mercury to the metallic state from their salts. The chloride and sulfate are the best-known compounds corresponding to this valency. The sulfate is isomorphous with ferrous and chromous sulfates.

The compounds corresponding to the trivalent oxide, V_2O_3 , show characteristic similarity to trivalent iron and chromium salts. With this valency also an increased tendency to form double salts is manifested. The halogen salts and sulfate with a large number of double salts, regular alums, are common. Oxalates, double oxalates, and salts of complex acids also occur.

With the next increasing step of valency, corresponding to the oxide VO_2 or V_2O_4 , the number of salts increases to a very great extent. This tetravalent vanadium appears to be the most stable base, as it forms salts with almost every inorganic and very many of the organic acids. Also the tendency to form double salts with organic as well as inorganic bases is appreciable. With this state of valency the acid character of the element begins to appear with the formation of vanadites, which are extremely readily oxidized to vanadates.

With the pentavalent stage of valency the number of compounds formed, as well as tendency to form double salts, further

increases. Also pentavalent vanadium very decidedly shows its acid character, with little tendency to form basic radicals. Its salts as a base with acids are comparatively few. The oxide V_2O_5 plays an important part in the technical chemistry of vanadium, as it has been the starting material for the manufacture of almost all vanadium compounds. It can be prepared in a perfectly pure state by calcination of ammonium vanadate. Obtained in this way it consists of extremely beautiful yellow-red crystals about 3 to 4 cm. long and 2 to 3 mm. wide, which readily melt at about 655° to 660° C. This oxide is the anhydride of three different acids, ortho-, meta-, and pyrovanadic acids, corresponding to the phosphoric acids. The number of vanadates formed from these three acids with inorganic and organic bases is overwhelmingly large.

Hexavalent vanadium is known to exist in the form of per-vanadic acid, HVO_4 , and its corresponding salts, which are little known.

This cursory knowledge of the activity of vanadium in forming large numbers of compounds with widely different properties and acting as a base or acid with change of valency, or even with the same valency, will help us to realize some of the difficulties in the technical operation of processes for extraction of the metal from the ores and of the large losses in recovery suffered in the earlier days of the industry. The realization of this fact was necessary, for instance, in the selection of a leaching agent for a particular mineral, which may have its vanadium content in a certain valency stage, or in the bringing of such vanadium content by pre-roasting, etc., to the valency state suitable to the leaching medium used, or in the selection of a precipitating agent, keeping the solution during precipitation in the right valency condition, or in selecting the right fluxes and refractory lining during the reduction of a certain valency vanadium compound to the metallic state.

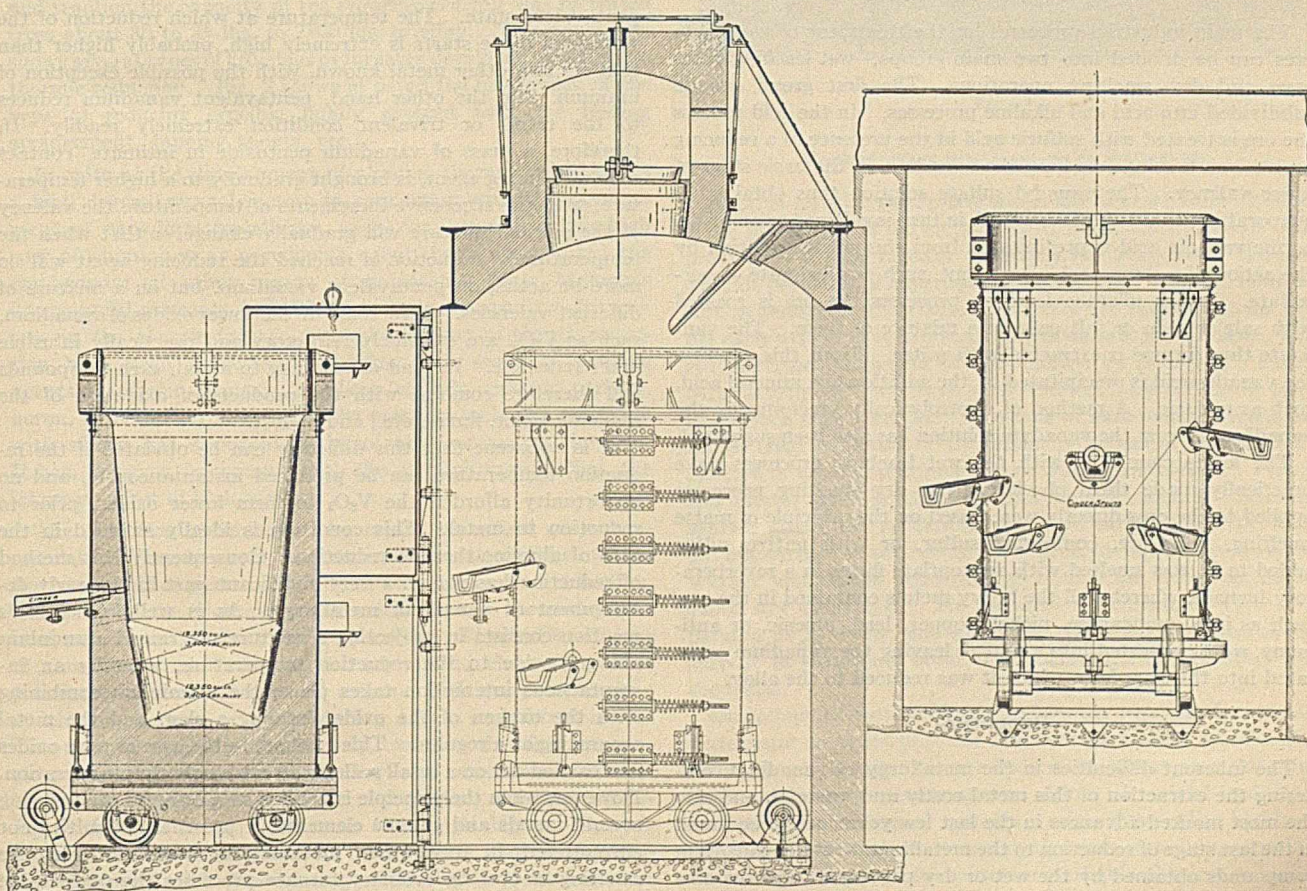


FIG. 2

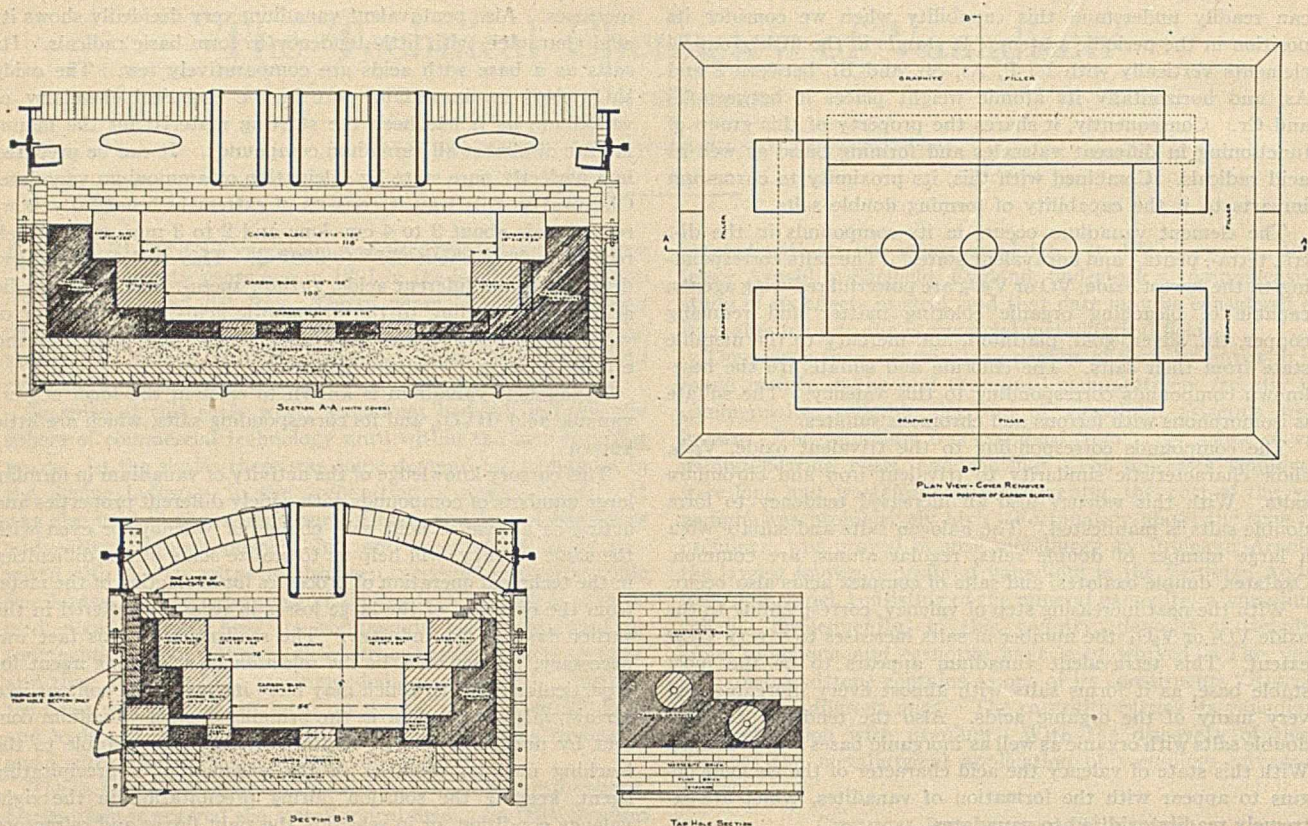


FIG. 3

TREATMENT OF VANADIUM ORES

The main industrial processes for the treatment of vanadium ores can be divided into two main groups; wet leaching processes and dry smelting operations. The first group can be subdivided into acid and alkaline processes. In the acid process the ore is treated with sulfuric acid in the presence of a reducing agent (iron turnings) to keep the vanadium in the basic stage of lower valency. The vanadyl sulfate solution thus obtained is evaporated to a sulfate cake, which in turn is calcined to an oxide, or the vanadic acid is precipitated from this sulfate solution by the action of a strong oxidizing agent, such as a chlorate or persulfate. In the alkaline leaching processes the ore is roasted with salt or soda or salt cake or a mixture of them. The vanadate thus formed is extracted with water. From this solution the vanadic acid is precipitated by the addition of a mineral acid, such as sulfuric. A method of electrolytically precipitating the vanadic acid from the vanadate solution has also been suggested.

The losses connected with the wet leaching processes have practically made them obsolete. The dry smelting processes applied to the ores directly were based on the principle of matte smelting. The ore, containing sulfur, or with native sulfur added to it, was smelted with appropriate fluxes in a reverberatory furnace, whereby all the heavy metals contained in the ore, such as iron, manganese, nickel, copper, lead, arsenic, or antimony, were converted into a matte, leaving the vanadium separated into the slag, from which it was reduced to the alloy.

REDUCTION

The inherent difficulties in the metallurgy of vanadium, rendering the extraction of this metal costly and wasteful, and also the most marked advances in the last few years, are to be found in the last stage of reduction to the metallic state of the vanadium compounds obtained by the wet or dry processes, or of the ores without such preliminary processes.

Vanadium usually exists in the materials to be reduced in the pentavalent state. The temperature at which reduction of the vanadium oxide starts is extremely high, probably higher than that for any other metal known, with the possible exception of uranium. On the other hand, pentavalent vanadium reduces to the tetra- or trivalent condition extremely readily. If, therefore, a mass of vanadium pentoxide in intimate contact with a reducing agent, is brought gradually to a higher temperature, with the successive increments of temperature the valency of the original mixture will gradually change, so that when the temperature of reduction is reached the reducing agent will no more be acting on pentavalent vanadium, but on a mixture of different valencies. Now some of the lower oxides of vanadium, such as V_2O_4 , are extremely refractory and practically infusible and irreducible. Instead of reducing to metal, such compounds will therefore combine with the products of oxidation of the reducing agent, fluxes, etc., and be lost.

It is apparent that this difficulty can be obviated if the reduction temperature can be produced instantaneously, and no opportunity afforded the V_2O_5 to form lower oxides, prior to reduction to metal. This condition is ideally satisfied in the case of aluminothermic reduction. Consequently this method of reduction has played a very significant part in the early development of vanadium metallurgy. As is well known, this reaction consists in subjecting a mixture of grained aluminium and an oxide to the reduction temperature, whereby an instantaneous interaction takes place, the aluminium combining with the oxygen of the oxide, forming a slag, and the metal separating as a regulus. This method, in the case of pure oxides and carried out on a small scale, is an extremely simple operation. However, when the principle is applied to a complex ore carrying several metals and gangue elements, it presents difficulties not encountered in any other metallurgical operation. In the smelting of ores by ordinary furnace processes the undesirable elements are eliminated by the production of a slag with suitable

fluxes. We know that for the production of such a slag, besides the chemical constituents, the physical conditions in the furnace play a big part. We therefore have, for example, a close temperature control of the operation, and also provide delicate means whereby we can control temperature to a very fine degree. In the aluminothermic reduction of complex ores we are working without the aid of such extraneously controllable physical means. The temperature is dependent only on the chemical reaction taking place, and consequently mainly on the amount of aluminium oxidized per unit of time. This amount, however, is governed by the constituents of the ore subjected to reduction. Fluxes are added to slag off the impurities. These fluxes retard the temperature of the reaction if they form an endothermic slag. The means employed to control at will the aluminothermic reduction of complex ores consist in (1) adding highly oxygenated compounds, such as sodium nitrate, which increase the oxygen content of the mixture without adding any metallic constituents in the alloy, (2) increasing the temperature by increasing the rate of feed of the mixture, (3) making the particles of the constituents finer, or (4) increasing the scale on which the reaction is carried on so that with large masses treated there will be an accumulation of heat energy stored as the reaction continues. To summarize these remarks it may be said that in the calculation of the mixture for reduction such a balance has to be found among the ingredients as will produce not only the right compounds in the slag and the right elements in the metal, but also the right amount of exothermic energy per unit of time, capable of keeping such slag and metal in the perfect fluid condition necessary for their separation. It is easy to see that this reduction process presents problems not ordinarily met. In the development of the vanadium industry it has been worked out to an extent as to form practically a new branch of metallurgy.

Fig. 1 shows diagrammatically the evolution of this process, where for the purpose of obtaining better control of temperature and reaction the capacity of the reducing crucible was increased from about 30 to 35 lbs. to 7800 lbs. of alloy. This figure also shows several types of crucibles or furnaces developed for aluminothermic reduction. Fig. 2 shows in detail the mechanism of the type of reducing crucible finally evolved with the feeding arrangement, tapping spouts, etc.

In spite of the development of aluminothermic reduction to a high degree, several factors in connection with the development of vanadium metallurgy, such, for instance, as the high cost of aluminium as a reducing agent, have necessitated the employment of other means of reduction. Since Moissan's unsuccessful attempts in 1893-94 to reduce vanadium by carbon in the electric furnace, several processes of electric reduction have been suggested, involving such metallic reducing agents as silicon, manganese, silicon carbide, calcium carbide, boron, or boron carbide. Of these processes only the reduction with silicon has appeared to be of any commercial interest. It has, however, in common with the aluminium reduction, the inherent defect of high cost.

The reduction of vanadium by means of carbon on a commercial scale has, however, been successfully accomplished within the last couple of years. The theory of instantaneous reduction, which made the aluminium reduction process successful, has been transferred to the electric operation. Physical conditions of aluminothermic reduction are reproduced electrothermally, principally a localized zone of extreme high temperature into which the mixture of ore, reducing agent, and fluxes is fed. This mixture reacts instantaneously, owing to the high temperature, is converted into slag and alloy, and passes out of the reacting zone to make room for the next portion of mixture arriving in the high temperature zone. The high degree of heat is obtained by the employment of high voltage and current density, combined with close spacing of electrodes, producing more or less a blow-pipe effect. The mixture is fed continuously in

the hottest part between the electrodes. The furnace is a three-phase rectangular furnace with a water-cooled cover, furnished with water-cooled bushings for three 12-in. graphite electrodes. The mix is fed in the furnace through water-cooled bushings in the top of the cover by means of continuous automatic feeders, and the metal and slag are tapped off by means of appropriate spouts.

Fig. 3 shows a sectional diagram of one 4000-kw. furnace. Fig. 4 shows the general exterior arrangement of the furnace installation.

VANADIUM ALLOYS

Vanadium has also entered the field of nonferrous metallurgy, and several alloys have been marketed for use in the nonferrous industry. A cuprovanadium, an aluminovanadium, a manganovanadium, and a cupromanganovanadium are commercial alloys. The exploitation of vanadium in the nonferrous industry is, however, comparatively in its infancy and furnishes a fertile field for metallurgical research.

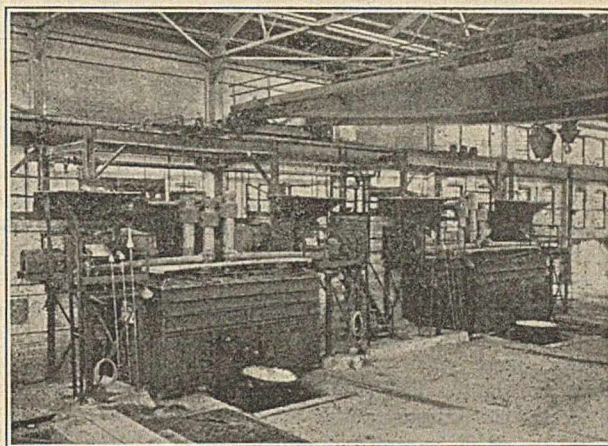


FIG 4

POSSIBILITIES FOR VANADIUM RESEARCH

Another metallurgical phase which has received little attention is the production of the metal itself without being alloyed. The production of pure metallic vanadium has been one of the most difficult problems of experimental chemistry. Its high temperature of reduction and chemical activity are responsible for this. All early attempts to produce pure vanadium have failed. Roscoe undertook reduction of the chloride by hydrogen. Setterberg attempted reduction with sodium. Goldschmidt failed to produce pure vanadium by means of aluminium. Weiss and Aichel tried reduction of the oxide by means of *Mischmetal*, a mixture of cerium, lanthanum, and other rare metals. Prandl and Bleyler failed in reduction with metallic calcium. Ruff and Martin attempted reduction with pure carbon. Cowper-Coles did not succeed in producing pure metal by aqueous electrolysis. Werner von Bolton attempted to obtain the metal by the so-called dry electrolysis. He prepared a filament of V_2O_5 using paraffin as a binder, and subjected this filament to the electric current in vacuum in order to dissociate the oxygen away from the metal.

On account of the inability to prepare the pure metal, naturally, statements as to its physical properties are very vague. Any future developments as to methods of preparing pure vanadium might prove of great commercial value. It might lead to investigations of alloys of vanadium with some other highly refractory metals such as tungsten, titanium, uranium, tantalum, etc., which alloys might possess remarkable physical properties useful in the arts.

Apart from the metallurgical side, vanadium has suffered very little technological development. An element as chemically active and as remarkable in its varying properties as vanadium would undoubtedly find useful application in chemical technology. As an example may be suggested its use as an oxidizing catalyst in the manufacture of perchlorates and perborates, and in several organic reactions. The use of vanadyl chloride as reducer in place of stannous chloride, and of its oxygenating compounds as a bactericide in water purification may be mentioned. The strong physiological activity of vanadium will also some day be utilized in the manufacture of compounds similar

to the arseno compounds, such as salvarsan. It would appear that an element capable of easy transference of valency as vanadium would open some field of research in its application to the use of electric cells, primary or secondary. The potential difference between the low and high valency compounds as measured by Marino seems to indicate that a research in this direction might be very fruitful. It is clear from these few examples that the chemical development of vanadium is still ahead of us, and it is to be hoped that its success in steel metallurgy will be the factor toward its wide application in other branches of technology.

Can We Afford the Ford?¹

By George Granger Brown

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

OF the 11,000,000 motor vehicles in the United States about 5,000,000 are Fords. If each Ford covers annually 5000 mi., we have 25,000,000,000 Ford miles per year. At an average of about 17.5 mi. per gal. this means a consumption of over 1,400,000,000 gal. of gasoline, more than one-fourth the total production of this country. Even a small saving in the fuel consumption of Ford cars alone is well worth the effort. Every general increase of 10 per cent in the efficiency of Fords means more than 140,000,000 gal. of gasoline saved annually for future use, more than \$30,000,000 to help pay the income tax, or, if you have the sales point of view, 75,000 more Fords sold per year.

The tests described in this paper indicate that the above estimates based on a saving of 10 per cent are very conservative—in fact at least 25 per cent increased mileage should be expected by making the slight changes in equipment suggested.

In making comparative tests on motor cars the utmost care must be taken to maintain all conditions, except those purposely varied, as constant as possible; otherwise the results are absolutely worthless. It is possible to obtain anywhere from 5 to 35 mi. per gal. with the same standard equipped Ford touring car, depending entirely upon the conditions under which the car is driven. In one case the car was driven through very heavy city traffic in cold weather by an "experienced" but very inexperienced driver, in the other case the car was driven by a very careful expert driver, at a constant speed of about 10 mi. per hr. on a level concrete highway, on a hot humid day. The careless driver used a rich mixture, the careful driver drove a hot engine with a very lean mixture—so lean that the engine would backfire when an attempt was made to accelerate.

For the present discussion it will be convenient to consider the over-all efficiency of a motor car as consisting of two factors, the efficiency of the power plant, and the drag of the chassis and body. The power plant efficiency is determined by the design of the engine and transmission, and the effectiveness and efficiency of the ignition and carbureting systems. The drag, or dead load, of the chassis and body is roughly a function of the car weight. In order to get the best possible results it is neces-

The average Ford touring car, driven under average conditions, gives not more than 17.5 mi. per gal. Compared with other cars it should give 24 mi. per gal.

One cause for this inefficiency is the present carbureting system, which can be so improved that the average Ford, driven under average conditions, will give 25 mi. per gal. and operate as economically as more expensive cars.

If this one improvement were applied to all the Ford cars in this country, 400,000,000 gal. of gasoline would be saved annually.

sary that all of these factors receive the most careful attention. The high cost of fuel in Europe has forced European manufacturers to consider these factors, and they have brought forth a number of very light cars equipped with efficient power plants of 12 to 20 h. p. These cars will run from

35 to 60 mi. per gal., depending upon conditions. Because of the low price of gasoline in the United States our motor cars are not designed for maximum economy. We have light cars with inefficient power plants and some cars with efficient power plants handicapped by a 4000- or 5000-lb. mass of dead weight.

In order to make intelligent comparisons of the relative operating economy of different cars, the variable weight and different designs must be reduced to a constant common basis. This can be done in a very satisfactory manner.

The wind resistance of all cars is practically the same. The rolling resistance, and particularly the force necessary for acceleration, is directly proportional to the weight of the car. The efficiency inherent in the power plant varies inversely as the displacement of the engine per unit of distance traveled.

These factors may be represented as follows:²

N = Number of cylinders
B = Bore, in in.
A = Area of bore, sq. in.
S = Stroke, in in.

H. p. = Horse power, $\frac{B^2N}{2.5}$

D = Total displacement, $\frac{ANS}{4}$

R = Gear ratio, rear axle

T = Tire

Wh = R. p. m. rear wheel @ 1 mi. per hr., $\frac{1056}{\text{Tire dia.} \times \pi}$

M = R. p. m. motor @ 1 mi. per hr., Wh × R

Wt. = Weight of car, in lbs.

C = Economy constant, $\frac{1000}{\sqrt{DM(1000 + \text{Wt.})}}$

G = Mi. per gal. under reasonably efficient operating conditions, $\frac{5200}{\sqrt{DM(1000 + \text{Wt.})}}$

The accompanying table shows the application of this formula to a number of standard cars produced in 1921.

This table is intended simply as an estimate of the miles per

¹ See also C. T. Myers, *Trans. Soc. Automotive Eng.*, [2] 9 (1914), 122, and *Soc. Automotive Eng. Bull.*, 8 (1915), 257.

Chemistry in the Senate

Importance of the Science Emphasized by Prominent Senators

(Excerpts from CONGRESSIONAL RECORD of August 17, 1922)

ON August 17, 1922, in discussing the Bursum Amendment, several senators spoke in favor of it. Senator Bursum of New Mexico in presenting the amendment began by saying:

Mr. President, the serious question confronting the country at this time, which prompted the introduction of this amendment, is whether the dye industry of this country shall be permitted to live, whether it shall be preserved, or whether we will permit it to go on the rocks, and depend upon Germany, as we did prior to the war, for our supply of dyes.

Senator Sterling of South Dakota, after declaring himself in favor of the amendment and explaining his preference for an embargo, said:

But, thinking that the embargo may not carry in the Senate, I am in favor of the amendment of the Senator from New Mexico.

I want to call attention just briefly to two or three facts and then cite some authorities which I think ought to have a controlling influence in this discussion.

It has been charged, of course, that there was great danger of a combination; that there was an actual combination between the dye-industry people. I have the honor of being a member of the sub-committee of the Judiciary Committee which investigated the dye industry. I was unable to hear all the testimony; very much of it I could not hear because of other pressing duties, but that which I did hear convinced me that there was no combination whatsoever among the various dye industries in this country. Indeed, the witness most relied upon by those who were asserting that there was a combination or monopoly admitted that there was the sharpest competition between the various companies engaged in the production of chemicals and dyes. That witness was Mr. Metz.

He then continued, citing a number of authorities such as Mr. James Morton, chairman of the Scottish Dyes, Ltd., to free trade members of Parliament, and Mr. Taussig, formerly a member of the Tariff Commission. He concluded:

Mr. President, I think I have not much more to add. I feel that interest in this very great and important industry. It has done so much within the short time it has been in existence since the beginning of the war, produced so much of wealth for the United States, given employment to so many thousand workmen, skilled and unskilled, in the United States, it seems to me that as American citizens, with pride in our industrial development, we should maintain and encourage it in the highest possible degree.

Senator Ransdell of Louisiana then spoke convincingly as follows:

Mr. President, I favor strongly the amendment of the Senator from Arizona. It seems to me, sir, that it has in it more possibilities for good to America and the world than any other feature of the bill. In considering this amendment we must bear in mind how necessary it is to establish and maintain a strong chemical industry in America, how essential this industry is for our welfare, our national defense, and, in a more important way, our public health.

The Germans, through their investigation of coal-tar products, have developed some marvelous remedies as an incident to the dye industry. They discovered and placed on the market salvarsan, which cures one of the most loathsome and terrible diseases that ever afflicted the human race. They discovered novocaine, one of the greatest deadeners of pain known to science, wonderful in that it is a nonhabit-forming drug, a most beneficial thing. Many other very helpful drugs have been developed by the efforts of the German chemists in connection with coal tar.

I cannot believe, sir, that the wise men of Germany have even scratched the surface of the possibilities of the coal-tar industry. Coal, sir, was made by the great Chemist of nature, how many years ago none of us know, and in its manufacture

everything that grows out of the ground, I imagine, was used, the most exquisite flowers, the sweetest balsams, the most healing plants and herbs of every kind and sort, and vast forests of giant trees. Coal furnishes more commodities for the use and health and comfort of mankind than anything I know of. The wonderful violet and rose perfumes which our ladies use are manufactured from coal. Saccharine, which is five hundred times as sweet as sugar, is manufactured from coal. All the beautiful dyes we admire so much are manufactured from coal. I could tell about many wonderful things, but have not time or opportunity to do so.

It seems, sir, that we should encourage in America in every possible way this enterprise which the Germans have set on foot and from which so much benefit has come to mankind. Does anyone believe that Germans have all the wisdom of the world? Does any American doubt that our composite American population is as wise and contains as smart people as Germany? Does anyone doubt that under proper encouragement American chemists will develop just as many valuable things from coal tar as have the Germans? As the German chemists have discovered novocaine and aspirin and salvarsan, why cannot American chemists discover remedies for cancer and leprosy and that most fatal of all diseases—tuberculosis? Great efforts to that end have already been made by American chemists. Let us encourage them in every possible way. American doctors have in the last 25 years demonstrated that they can do wonders in treating diseases. American doctors discovered the cause of hookworm and pellagra and treated them successfully. They found out that the Stegomyia mosquito was the cause of yellow fever and have practically eradicated that dread disease throughout the world. All we need to do, sir, is to give proper encouragement to American chemists and they will, in my judgment, prove by their medicinal discoveries just as beneficial to America and to the world as ever the Germans have been, and as helpful to suffering humanity as their brethren in the medical profession, for I cannot believe that all the secrets in the interest of health hidden by the Architect of the Universe when He created coal have yet been unearthed. There are many secrets still hidden. Let us discover them, or at least let us try to discover them. This is only one phase of the case.

Many people say, and I agree with them, that the next war, if war must come—and unfortunately it has always come to the world—will be a chemical war. America must be ready for it at home. She must develop her own chemical resources and not depend upon other countries. She must create a great chemical industry, and make all known combustibles in order to be prepared for a possible war.

This matter of national defense is only one of many important things which can come from the development of the coal-tar industry. I sincerely hope, sir, that the amendment will be agreed to.

He concluded his remarks by reading into the RECORD an excellent letter from Councilor Charles E. Coates of the Louisiana Section of the AMERICAN CHEMICAL SOCIETY.

Then followed remarks by Senator Wadsworth of New York which we quote in full:

Mr. President, as a part of my remarks, I ask that a letter written by the Secretary of War to the chairman of the Committee on Finance, the Senator from North Dakota [MR. McCUMBER], may be read by the Secretary.

THE PRESIDING OFFICER: Without objection, the Secretary will read as requested.

The reading clerk read as follows:

WAR DEPARTMENT
Washington, August 15, 1922

CHAIRMAN UNITED STATES SENATE FINANCE COMMITTEE,
Senate Office Building, Washington, D. C.

MY DEAR SENATOR McCUMBER:

On July 26, 1921, I wrote your committee, calling attention to the fact that the Fordney tariff bill would not protect the American organic chemical industry from destruction by German competition. Allow me to reiterate

the importance of the preservation of this industry to the country from the standpoint of national defense.

The dye industry is the backbone of the organic chemical industry, on which all Governments are dependent for their high explosives, their medicines, and other materials. Inasmuch as the coal-tar industry, which is the basis of all dyes, is also the basis of all high explosives and of synthetic medicines, it is of vital importance to preparedness that the dye industry be developed to the fullest possible extent in this country. The use of explosives will be far greater in any future struggle than in the World War.

Notwithstanding that from 1914 to 1917 our great steel industries and our rapidly developing chemical industries had been working feverishly to increase their facilities to supply ammunition, guns, and rifles to the Allies, it was more than a year after we entered the war before those industries were able to supply ammunition, guns, rifles, etc., to meet the American needs. Even then our chemical industry was so undeveloped in 1917 that it was necessary for the Government to build large high-explosive plants and powder factories.

Germany realizes the importance of predominance in organic chemical industries as a most valuable means of preparedness and has formed of them one great trust. The German trust can produce dyes and similar material so much cheaper than the Americans produce them that no ordinary tariff can prevent the destruction of the American industry, which will thereby cripple the whole organic chemical industry.

It is, therefore, urged that the dye-control provisions of the emergency tariff act of 1921 be extended another year to give the industry a chance to stabilize and to enable conditions in the dye industry to be carefully observed and the products determined which should be protected in order to firmly establish that industry in the United States.

Very truly yours,

JOHN W. WEEKS,
Secretary of War

MR. WADSWORTH: Mr. President, it is apparent, of course, that the concluding paragraph of the letter of the Secretary of War is not applicable to the amendment which is now pending because in that paragraph the Secretary urges the continuation of the selective embargo at present in force. I thought, however, it would not be amiss that the letter of the Secretary in which he discusses from the standpoint of the national defense the value of the organic chemical industry be placed in the RECORD at this time. I think that not even the most suspicious-minded man will accuse the Hon. John W. Weeks of being impelled by unworthy motives when he urges upon Congress the consideration of the chemical industry in connection with the defense of the Republic.

It is quite possible, Mr. President, that a good many Senators do not feel as deeply upon this subject as do I. Perhaps I feel too deeply upon it; I do not know; but, such as my feelings are, I intend to express them upon this occasion as briefly as possible.

From what I have been able to learn of the history of organic chemistry in this country, especially in the dye industry, prior to our entrance into the World War, during our participation in the war, and since the war, I am convinced that long before the United States actually declared a state of war the German Government and the cartel were in effect, although slyly, waging war against the peace and the safety of the people of the United States. We did not wake up to that situation until we ourselves got into the fight. The letter of the Secretary of War points out very briefly—all too briefly, according to my view—but sufficiently for the purposes of this discussion the predicament in which this Republic of ours found itself when we were called upon to engage in our own defense.

Manipulations of the German cartel in the matter of patents, the immense influence, politically and otherwise, which they maintained in this country before the European war must now be known to every sensible man. Their effort was deliberate; it was skilful, and it was successful up to a certain point. That effort was directed toward making and keeping the American people as helpless as possible in the event of any great crisis overtaking them in which the German Government might be a party.

We went into the war and we learned the lesson at the cost of billions of dollars and many thousands of lives. We participated in the great victory and at the conclusion of the contest we asked for no territory; we asked no reparations; we asked for nothing of value to be taken from the vanquished and we received nothing. The only thing which has come to the people of the United States of material value as a result of their efforts and sacrifices in the Great War is peace and security in the future and the guaranty of self-maintained public health; not one other thing or opportunity of a material character has come to this great people of ours out of that war.

We have the opportunity, as the result of the contest, an opportunity seized upon legally to maintain our public health

with our own resources and without depending upon any foreign government or any foreign cartel, corporation, or trust. We have secured the opportunity—and have secured it legally and properly as a result of our sacrifice and our efforts in the war—to maintain our national defense without depending upon any other nation, government, trust, or cartel of any kind whatsoever. That is the prospect which confronts the American people to-day.

Mr. President, I am not surprised that far-reaching efforts have been exerted in this country for the last two years once more to reduce us to that condition of comparative helplessness in which we dreamed and dreamed and dreamed in 1916. I am well aware of the influences which have been brought to bear here in Washington; I am well aware of the source of those influences; I know perfectly well that if this cartel can once more establish its domination over the organic chemical industry of the United States, such as it enjoyed prior to our entrance into the war, the enemies of America, actual and potential, will rejoice.

I question not the motives of Senators who do not see this question as I see it; without doubt they are sincere; but it passes my comprehension how they can fail to read the signs of the times. If there ever was a deliberate attempt to break down, to undermine, to weaken the power of American self-defense, it has been made in connection with the American organic chemical industry.

It does not do, Mr. President, in discussing this matter, to drag the names of American citizens into the discussion and accuse them of dishonest motives because, forsooth, they take an interest in the perpetuation of this chemical industry here in America. It does not do, Mr. President, to bring inferences and insinuations against Francis P. Garvan; not by any means. I care not what his politics are; I understand he is a Democrat; I have known him since 1895 and known him well. He is an honest man, and he has no thought in his mind or motive in his heart except the safety of this country. It does not do to bring unfair inferences and insinuations against men like Otto Bannard, of New York, who is one of the trustees of the Chemical Foundation, for he is an honest man, with no thought except the safety of his country.

I shall not discuss upon this occasion the wisdom or the unwisdom of the policy adopted by the last administration in the handling of the patents covering the dyes through the Chemical Foundation as trustee; that is not a part of this discussion; but I know full well, if I know anything about the psychology of this situation, that the attack upon the Chemical Foundation had a most material influence upon the votes cast on the question of the tariff on dyestuffs. It is for that reason that I deplored it at the time, although not publicly, for I had no opportunity to do so, but I deplore it now. It is not the question at issue.

Mr. President, as I said in my opening sentence, I feel deeply on this question. I believe that there is involved in it one great issue: America safe against attack from without and safe in the matter of public health, or America dependent upon some outside power and influence in the matter of its self-defense and in the matter of its public health.

This organic chemical industry lies at the bottom of nearly everything we use. I firmly believe that the progress of the race from now on will be measured more by the progress in organic chemistry than in any other human effort. I believe that in organic chemistry lies the solution of the secrets of the past and of the future. I believe that its establishment and maintenance in this country, even under an embargo, mean the happiness, the progress, and the security of 100,000,000 people. No rate of duty will frighten me and no embargo will frighten me.

I notice that England has put an embargo against the importation of dyestuffs. I notice that France has done the same thing. I notice that Italy has done the same thing. I notice that Japan, if she has not already done so, is about to do so. They have awakened to the significance and the importance of organic chemistry. I pray that the time will come when American public opinion will come to an appreciation of what organic chemistry means, of what research means, in the way of progress. We have been interested as a people in the development of material resources—the digging of iron and coal from the ground, the raising of crops upon the surface, and the engaging in transportation and other forms of commercial effort. As a people we have paid little attention and given little encouragement to scientific research, but, Mr. President and Senators, the progress of the future depends upon scientific research. It is the man working in the chemical laboratory who is to blaze the way for human progress.

I want to see the chemical laboratories of this country multiplied again and again. They cannot be multiplied, they cannot be maintained, no student will attempt to attend their courses unless there is a chemical industry in which those students upon graduation may find a career.

The two things—research in the laboratory and the successful conduct of a chemical industry—go hand in hand. Neither can proceed without the other.

I regret that the Senate voted down the selective embargo. I think it made a mistake. I was in the minority upon that proposition. That is my first choice as a remedy. The Senator from New Mexico [MR. BURSUM] has offered an amendment which, in my judgment, is next best. It will give some chance, at least, for the survival of this industry of ours, which already bids fair to be able to meet the demands of our people, although it has only been devoted to its task for three or four years, and research was almost unknown in this country. I think that industry will get a decent chance to survive under the amendment offered by the Senator from New Mexico. Feeling as I do upon this question, feeling that it is vital to the security and the happiness and the contentment of this great Nation, I beg for its adoption.

Senator Lodge of Massachusetts, after questioning Senator Smoot regarding the time required for making investigation on comparative costs in the United States and elsewhere, spoke briefly but with great emphasis and finality:

MR. LODGE: I have here a letter dated August 16 from the Tariff Commission, which I shall ask to have printed in the RECORD, and in which this statement is made:

The time required for such an investigation is uncertain, but from experience gained in other chemical investigations we believe it will require from 8 to 10 months to make a satisfactory report on the subject.

During those 8 or 10 months, of course, the dyes would come in.

Mr. President, I did not mean to enter into this discussion. I took no interest whatever in the matter of rates or whether

we keep out all other dyes or not. I have but one single interest in the question, which is derived from some years of experience in the Senate. I endeavored back in 1909, in conjunction with the Senator from Utah, to get some protection which would tend to give us an independent chemical production. We failed. We got into the war. We had no chemists who could furnish us with explosives and later with the gases. It was the same in England, which was then believing in the phantom of free trade. She found herself in the same condition. No one can possibly tell what that disadvantage, which weighed down upon both England and the United States, cost us in men, money, and time in the winning of the war. I made up my mind that, so far as I was concerned, I would use every effort in my power to see that the United States was never left again defenseless in that way.

I voted for the embargo when it was proposed by the Democratic Party. I voted for it during the war. I continued to vote for it when it was continued when the Democratic Party had not yet gone out of power. I voted for it for the sole reason that I wished the country to be independent in the matter of organic chemistry. No matter what it may cost, it is something that is worth any price they choose to pay to make the country independent in that direction.

Mr. President, I voted for it again for the same reason. It does not weigh with me that the dyes can come in at this price or can come in at another price. I want to do what the other countries have done who have learned something from their experience. I want this country to see to it, by tariff or embargo or in any other way, that organic chemistry in the United States is put in a position where we shall never find ourselves in the condition in which we were before. I am speaking not in the interest of any industry. I have not been approached by anybody representing an industry in that respect. I know the interests that are here. I have heard of the representatives of the German importing interests rejoicing in the lobbies here when the embargo was beaten the other day. I have taken this long interest in it for these years for but one reason, and I vote for this provision to-night for but one reason, and that is national defense and safety.

Chemistry Courses at College of the City of New York

The members of the Evening Session Chemical Society of the College of the City of New York would like to call the attention of chemists and students of chemistry, who wish to increase their knowledge of the subject, to the excellent opportunities offered evenings by the Chemical Department of the College. Courses are given leading to the degrees of B.S. and Ch.E. Besides these degrees, a special departmental certificate is given to students who desire chemical knowledge only. To receive this certificate the student must complete Courses 1, 2, 3, 4, 11, 20, 33, 44, 50, 55, and 70, with an average of 80 per cent, and make a satisfactory report on some research problem the student has worked on Chemistry 100. Thus, this certificate indicates that the holder has a knowledge of the main branches of chemistry (with a very good scholarship rating) and some practice in research and should be of great value to any man.

The following courses will be given this fall:

CHEMISTRY 1-2. GENERAL DESCRIPTIVE CHEMISTRY. 6 hours per week. 2 terms. Laboratory deposit \$10 per term.

CHEMISTRY 3. QUALITATIVE ANALYSIS. 7 hours per week. 1 term. Laboratory deposit \$12.

CHEMISTRY 4. QUANTITATIVE ANALYSIS. 8 hours per week. 1 term. Laboratory deposit \$12.

CHEMISTRY 20. PHYSICAL CHEMISTRY. 7 hours per week. 1 term. Laboratory deposit \$8.

CHEMISTRY 33. ADVANCED QUALITATIVE ANALYSIS, mainly on rare elements. 12 hours per week. 1 term. Laboratory deposit \$14.

CHEMISTRY 44. ADVANCED QUANTITATIVE ANALYSIS. 12 hours per week. 1 term. Laboratory deposit \$14.

CHEMISTRY 50. ORGANIC CHEMISTRY, ALIPHATIC COMPOUNDS. 7 hours per week. 1 term. Laboratory deposit \$15.

CHEMISTRY 55. ORGANIC CHEMISTRY, AROMATIC COMPOUNDS. 8 hours per week. 1 term. Laboratory deposit \$20.

Besides these regular courses, two or possibly three special courses of interest to specialist and graduate student will be announced as follows:

CHEMISTRY 159. FOOD INSPECTION AND ANALYSIS. Dr. Breithut. Special practice in analysis of food products and drugs—as, milk, butter, cereals, beverages, etc., the sale of which is controlled by the city. Occa-

sional lectures and excursions in cooperation with the Food and Drug Inspection Laboratory of the Department of Health.

CHEMISTRY 269. ECONOMICS OF CHEMISTRY. 5 hours; lectures, library and seminar. Fee \$12.50. Dr. Breithut. The economics of production and distribution of chemical products, sources of new material, sources of energy, and conservation of waste. Study of consular reports and use of the Wolcott Gibbs, Chemists' Club, and New York City Libraries.

CHEMISTRY 146. TECHNICAL ANALYSIS. 8 hours of laboratory. (To be announced.) Analysis of coal, soap, paint, lubricating oils, greases, cements, asphalt, and other materials purchased by the city.

To students pursuing a degree, there is no tuition charge. Others will have to pay at a rate of \$2.50 per hour per week each term. For example, a 3-hour a week subject costs \$7.50 per term. Further information may be obtained by writing to the Evening Session Office, Room 226, College of the City of New York, Convent Ave. and 140th St., New York City. Registration for the fall starts Monday, September 18, at 7:00 P.M. First recitation, September 28. Students, especially for the special courses, are advised to register early, as these courses must have a certain minimum of students in order to be given.

Motion Picture Film Service

It has frequently been brought to the attention of THIS JOURNAL that professors, instructors, and others want to use moving picture films for instruction and for entertaining on many occasions, but are not familiar with the sources of obtaining films to suit their needs. Therefore, it is proposed to devote a small space each month to listing films which may prove of interest and value to our readers, including information as to source, terms, etc. We plan to begin this service with the November issue, and hope that it may prove to be of material assistance.

The Union Sulphur Company has bought from the Texas Exploration Company the sulfur deposits at Damon Mound, Texas, comprising about 215 acres estimated to contain over 14,000,000 tons of sulfur, and is to build complete mining, refining, and terminal plants.

AMERICAN CONTEMPORARIES

Beginning with this issue we shall occasionally publish intimate sketches of our prominent American contemporaries in chemistry. This plan has been inaugurated in response to the wishes of our younger people who have had no opportunity to know the personality of many men whose names are familiar to all chemists.

These sketches, then, will be short statements intended to portray something of the kind of men these chemists are, what they set out to do, and a little of what trend their life's work has taken. We

wish you could meet and talk with all these folk who have had such a guiding influence upon our science in America! But that may not be possible, and so we hope these sketches, prepared by close friends for us, may in some measure meet the need. The list has been made up with the help of our staff correspondents, but may be considerably extended.

Make it a point to meet these men of chemistry through our pages if you cannot in person. [EDITOR.]

Charles Frederick Chandler—Dean of American Chemists

PROFESSOR Chandler is the original exponent of the strenuous life. He was living a strenuous life as a professor in Union College and in preparation for his distinguished career as a chemist, the year Theodore Roosevelt was born.

Charles Frederick Chandler was born in Lancaster, Mass., December 6, 1836. He came from good old New England stock, attended the public schools in Lancaster and New Bedford, and studied at Lawrence Scientific School, Harvard. Ambitious to become a chemist and endowed by inheritance with Yankee pluck, he went to Europe on a sailing ship in the early fifties to continue his studies under the great masters: Hofstad, Wöhler, Gustave and Heinrich Rose, Weber, Dove, and Magnus. A doctor of philosophy from Göttingen, and a full professor in Union College, at the age of twenty-one!

The day after he cast his vote for Abraham Lincoln, Professor Chandler joined Professor Egleston and General Vinton in New York, to establish what is now the School of Mines, Engineering, and Chemistry, Columbia University. He served this great institution as professor of chemistry for forty-six years, and as administrative dean of the school, for thirty-three years. He led its development from a vacant room in the basement of the old Columbia College in Forty-ninth Street, to the present great architectural group of laboratories at Morningside Heights, and placed its graduates in charge of mining, manufacturing, transportation, and construction enterprises in every quarter of the world.

Professor Chandler's educational achievements were not limited to the School of Mines. His genius was directed to building up the College of Physicians and Surgeons, which he served as professor of physics and chemistry, and the New York College of Pharmacy, as professor of chemistry, and finally as president.

Yet his energy and versatility were not at an end. His greatest public service was in the application of his scientific knowledge and genius for organization to public welfare and health. As chemist and finally as president of the New York



C. F. CHANDLER

Board of Health, he investigated and regulated gas nuisances, offensive trades, sludge acid pollution, city slaughter houses, water and milk supplies, adulterated foods and drugs. He reformed tenement house plumbing, improved ventilation, reorganized street cleaning, and established the system of visiting physicians and free vaccination. He was a pioneer in pure food and drug legislation.

Dr. Chandler is America's first and most distinguished industrial chemist. His expert knowledge and advice made him an important factor in the building up of the sugar, petroleum, gas, photochemical, textile, electrochemical, chlorine, aluminum, and many other notable American industries. He invented and introduced the assay-ton system of weights used in every smelter in America. The title, "Dean of American Industrial Chemists,"

is his by unanimous consent.

Professor Chandler is the recipient of many honors, official, academic, public, and professional. He has represented the federal government on many important commissions. He has received honorary degrees from numerous colleges, including an anniversary degree from Göttingen, and that of Doctor of Science from Oxford. He is a member of the National Academy of Sciences, past president of the American Chemical Society, The Chemists' Club, and the Society of Chemical Industry. Last and most important of all, he is the recipient of the Perkin Medal "for such valuable contributions to applied chemistry that he has placed the entire world in his debt, and brought added prestige and dignity to the profession of which he is such a conspicuous ornament."

Twelve years ago, when Doctor Chandler retired from Columbia, he stated that "it is much better to withdraw from active service while one is in the full enjoyment of health and strength, than wait until the infirmities of age make it evident to all that one has outlived his usefulness." Fortunately for the chemical profession and its industrial dependents, this condition has not yet arisen. Professor Chandler may be found to-day at his desk in the offices of the Chemical Foundation, or at his library, actively and enthusiastically giving the touch of a master hand to the technical problems of American industries.

M. C. WHITAKER

SCIENTIFIC SOCIETIES

A. C. S. Division and Section Meetings

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY

The symposium on "Edible Fats and Oils," conducted jointly with the Division of Biological Chemistry, was a great success. The first portion, on the manufacturing and technical phases of the subject, was presided over by David Wesson, while that of a biological and physiological nature, presented in the afternoon, was conducted by R. Adams Dutcher. The papers on rancidity promoted much discussion. The two papers on the effect of shortening as used in the baking industry were much appreciated. The five papers on the biological study of the subject drew large audiences, about 90 being present at times. Seven papers on the program were read by title only, because of absence of the authors or incompleteness of the investigations.

At the next meeting of the Division a symposium on "Insecticides and Fungicides" will be held, and one year hence it is planned to have a joint symposium with the Fertilizer Division on "Fertilizer and Crops."

The officers for next year are:

Chairman: H. A. NOYES.

Vice Chairman: R. H. CARR.

Secretary: C. S. BRINTON.

Executive Committee: T. J. BRYAN, H. F. ZOLLER.

C. S. BRINTON, *Secretary*

DIVISION OF BIOLOGICAL CHEMISTRY

On Wednesday this Division joined with the Division of Agricultural and Food Chemistry in a symposium on "Edible Fats and Oils." The report of this very interesting symposium will be found in the report of the Division of Agricultural and Food Chemistry.

As Chairman H. B. Lewis was unable to attend the meeting, Secretary J. S. Hughes presided at the Thursday session and J. F. Lyman was elected secretary *pro tem*. At this session 21 of the 31 papers listed on the program were presented and discussed, the remaining papers being presented by title.

The following officers were elected for next year:

Chairman: J. S. HUGHES.

Secretary: W. V. BOVIE.

Executive Committee: H. B. LEWIS, Chairman, A. W. DOX, D. B. JONES, A. R. LAMB, J. F. LYMAN.

J. S. HUGHES, *Secretary*

DIVISION OF CHEMISTRY OF MEDICINAL PRODUCTS

In addition to the regular program of the Division, a symposium on "Development of American Synthetic Medicinals" was held. The papers and discussions in the course of this symposium indicated the rapid strides being made to establish a purely American medicinal chemical industry, not only by developing the manufacture of substances already known, but by producing new superior products as well.

After the meeting program the following officers were elected:

Chairman: EDGAR B. CARTER.

Secretary: E. H. VOLWILER.

Executive Committee: C. E. CASPARI, OLIVER KAMM.

E. H. VOLWILER, *Secretary*

DIVISION OF CELLULOSE CHEMISTRY

The Cellulose Section was given definite status as a Division and the first meeting on the new basis proved to be of unusual interest. Wednesday afternoon was devoted to a symposium on "The Nature of Wood Cellulose." The discussion was particularly spirited and participated in by a large number of members. The symposium on "The Adsorption of Salts by Cellulose" also aroused much interest. These symposiums

were so successful that many expressed the hope that others, on equally timely subjects, might be arranged for future meetings.

Of special interest to all members of this Division is the announcement of C. J. West, of the National Research Council, Washington, D. C., that, through the courtesy of the publishers of the various cellulose and paper magazines of the world, he is in a position to loan to members of the Cellulose Division current copies of practically any pulp and paper magazine, as well as articles on cellulose. He also offered to furnish photostat copies of practically any article on cellulose chemistry or pulp- and paper-making since 1909. This is a very generous offer and much appreciated by the members of the Division.

The Viscosity Committee of the Cellulose Division reported a method for the determination of the viscosity of cellulose ester solutions. This method was adopted as the tentative standard method of the Division. The details will be published in THIS JOURNAL and it is hoped that a number of laboratories will report on the actual working of the method at the next meeting.

The officers elected for the Division are:

Chairman: G. J. ESSELEN, JR.

Vice Chairman: L. E. WISE.

Secretary-Treasurer: L. F. HAWLEY.

Executive Committee: HAROLD HIBBERT, J. F. WAITE.

G. J. ESSELEN, JR., *Secretary*

DIVISION OF DYE CHEMISTRY

The meeting opened with a symposium under the leadership of R. E. Rose, on the subject of "Standardizing and Testing of Dyes." As a result of the discussion in this symposium a committee was appointed to consider the best methods of securing uniformity and correctness of results in testing of dyes as an aid to both manufacturer and user. R. E. Rose is chairman of this committee, and the other members are: L. A. Olney, W. M. Scott, J. Merritt Matthews, and J. A. Ambler.

The regular program included papers on the manufacture, properties, and application of dyes. M. L. Crossley's paper on the relation of chemical constitution and color attracted considerable attention.

Officers for the ensuing year were elected as follows:

Chairman: W. J. HALE.

Vice Chairman: R. E. ROSE.

Secretary: R. NORRIS SHREVE.

Executive Committee: L. A. OLNEY, L. F. JOHNSON.

R. NORRIS SHREVE, *Secretary*

DIVISION OF FERTILIZER CHEMISTRY

A special symposium had been arranged to bring out the modern trend in all branches of the fertilizer industry in the following directions: (1) Fertilizer Plant Construction; (2) Fertilizer Plant Operation; (3) Chemical Control in the Fertilizer Industry; (4) State Fertilizer Control; (5) Fertilizer Legislation; (6) Fertilizer Experimentation.

These papers described in an interesting manner the part chemistry has played in reaching the present high development of the fertilizer industry, the largest of the heavy chemicals industry. While it might at first seem that plant construction and operation are out of place in such a program, such is not the case as the relation between the type of construction and the operation and the method for the chemical control of such operation is very close and interdependent.

Several papers were presented on methods of analysis for the determination of phosphoric acid, nitrogen, and potash. Many of the possible errors in the application of these methods were discussed, together with precautions necessary to avoid them.

Several papers described and discussed fertilization experiments, the action of fertilizers in the soil and the relation of fertilizer to plant composition.

Some of the effects of the rational use of fertilizers, such as larger yields and better quality of crop, especially fruits, were described. It is becoming more apparent that the best

results in the use of fertilizers are obtained from the use of sufficient quantities of properly balanced, high-grade, complete fertilizers.

The officers of this Division were reelected for the ensuing year.

H. C. MOORE, *Secretary*

DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

The meeting of the Division was distinguished by two symposia in addition to the general papers, and a special discussion of Mr. Midgley's paper. The first symposium was upon "Automatic Process Control," the chairman of which was L. W. Parsons.

The second symposium was upon "Combustion," and was under the auspices of the Division's new offspring, the Section of Gas and Fuel Chemistry, with R. T. Haslam as chairman. Without doubt it was the most interesting and instructive symposium of the meeting. Further details concerning this symposium are reported by the Section of Gas and Fuel Chemistry.

Thursday morning the Division discussed Midgley and Boyd's paper entitled "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine." Keen interest in this subject was manifested and the discussion lasted nearly an hour. (See p. 894, this issue.)

The general papers covered nearly every phase of industrial chemistry. The grade of the papers was of a very high standard, and the frequent discussion showed that the authors were stimulating thought in their hearers.

The present active committees were continued.

The title of the symposium for the spring meeting at New Haven has not been decided upon as yet. "Agitation" has been suggested as a subject.

The attendance at the sessions of the Division was large. It reached as high as 350 and was considerably over 100 most of the time.

The following officers were elected:

Chairman: D. R. SPERRY.

Vice Chairman: W. A. PETERS, JR.

Secretary: E. M. BILLINGS.

Executive Committee: W. F. HILLEBRAND, EDWARD MALLINCKRODT, JR., F. M. DE BEERS, A. SILVERMAN, H. R. MOODY, C. E. COATES.

E. M. BILLINGS, *Secretary*

DIVISION OF LEATHER CHEMISTRY

The fourth meeting of this group had a program of 24 papers, all of which were read. In addition to the papers mentioned, a contribution was received from Dr. Edmund Stiasny, one of the most prominent leather chemists of continental Europe. The keynote of the program was the development of the fundamental principles of practical leather manufacture. Beginning with a series of papers on unhairing and bating, the entire processes of both chrome and vegetable tanning were covered. Explanations were given of the mechanism of the existing processes, together with the results of scientific investigations, leading to the development of new processes as well as the importance of the old ones. A feature of the program was the gelatin symposium in which the physical chemistry of gelatin was discussed. This symposium attracted a capacity audience. A paper by Dr. Jacques Loeb resulted in considerable discussion, in which Sheppard, Bogue, Davis, and Wilson participated.

The following officers were elected for the ensuing year:

Chairman: J. ARTHUR WILSON.

Vice Chairman: CHARLES S. HOLLANDER.

Secretary: ARTHUR W. THOMAS.

Executive Committee: F. P. VEITCH, C. R. MCKEE.

ARTHUR W. THOMAS, *Secretary*

DIVISION OF ORGANIC CHEMISTRY

Of the 62 papers on the program, 57 were presented. Because of the length of the program, the presentation of papers was limited to 7 min. and the discussion of each paper to 3 min. The time limits were enforced with the aid of a "kodak timer." The actual time taken for the presentation of the papers and discussions was 8.5 hrs. The Division voted to continue the abstract service which had been inaugurated this year. The

cost of this service for the two meetings was about \$100 for 400 members. A committee was appointed to consider the necessity and desirability for changing the method of presenting papers. It was decided that it would be inadvisable to make any change at the present time. It was also decided to arrange a symposium on some suitable subjects for the New Haven meeting.

The officers elected for 1923 were:

Chairman: FRANK C. WHITMORE.

Secretary and Vice Chairman: R. R. RENSHAW.

FRANK C. WHITMORE, *Secretary*

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

The Division of Physical and Inorganic Chemistry held four sessions at which a very interesting program of 59 papers was presented.

After considerable discussion it was voted that the executive committee be instructed to consider and decide before the New Haven meeting as to the possibility of charging \$1 or \$1.50 dues and using the proceeds to send brief edited abstracts of all papers to all members in advance of the meeting. About 30 members signified their desire to be enrolled on this basis. All those desiring to have their names added to the list will please communicate with Secretary Graham Edgar, at the University of Virginia, Charlottesville, Va.

A committee was also appointed to canvass the Division for nominations for members of the board of editors of the new *Journal of Physical Chemistry*. After receipt of their detailed report, a list of names was recommended to the Advisory Committee of the SOCIETY.

The following officers were elected for the coming year:

Chairman: ROBERT E. WILSON.

Secretary: GRAHAM EDGAR.

Executive Committee: FARRINGTON DANIELS, G. H. ELLIS, JAMES KENDALL, E. B. MILLARD, R. G. VAN NAME.

R. E. WILSON, *Secretary*

DIVISION OF RUBBER CHEMISTRY

The Rubber Division had without doubt the most interesting meeting in its history. The attendance was never below 100 and often ran as high as 140. The outstanding features were the presentation of high-speed hysteresis data on rubber, by W. W. Vogt, and the partial disruption of our present theories of organic acceleration of vulcanization, by F. G. Breyer. Details of a machine and results obtained on various compounds were given by Mr. Vogt, which showed hysteresis losses in rubber when developing from 40 to 400 cycles per minute. This is approximately the number of cycles developed in an automobile tire running from 4 to 40 miles per hour. The results show variation from former data and throw light on the physical behavior of rubber in tires. Mr. Breyer presented considerable data on the relation of cure to particle size of compounding ingredients. We have heretofore considered zinc oxide incapable of acceleration, but attributed a good reinforcing effect in rubber to its use. Well-established data given by Mr. Breyer show that extremely fine zinc oxide is a fairly rapid accelerator, and when an ordinary organic accelerator is used in conjunction with it, the effect of the organic accelerator is merely to add tensile strength but not to shorten the cure. Interesting data on the structural reactions of organic accelerators were presented in different papers by Bedford, Scott, Gray, and Sebrell, as well as other valuable papers dealing with the influence of different ingredients in vulcanized rubber.

Committee work on research physical testing and standardization of chemical analysis is being continued, both committees presenting reports showing fine progress. A committee consisting of E. B. Spear, N. A. Shepard, D. F. Cranor, C. W. Sanderson, and H. V. Bloom was appointed to present standard testing formulas to the Division for consideration.

Officers were elected as follows:

Chairman: W. B. WIEGAND.

Vice Chairman: E. B. SPEAR.

Secretary: ARNOLD H. SMITH.

Executive Committee: C. W. BEDFORD, D. F. CRANOR, G. S. WHITBY, H. L. FISHER, N. A. SHEPARD.

ARNOLD H. SMITH, *Secretary*

DIVISION OF SUGAR CHEMISTRY

In the absence of S. J. Osborn, who was detained by illness, the meeting was presided over by F. W. Zerban, vice chairman of the Division. The session as a whole was one of the best the Division has held. The attendance, while not as large as at some previous meetings, was good. The interest manifested in technological papers was greater than usual and foreshadows an increasing activity in the Society by the technical men of the industry. The program covered a wider range of subjects than usual.

Among the papers presented were a number of importance in precise analytical sugar work, the subject of reducing sugars being prominent. The subject of decolorizing carbons, recently of importance to the industry as a whole, was given considerable time and brought out much discussion. In addition, papers on bacteriology, factory operation, and laboratory apparatus were presented.

The following officers were elected for the coming year:

Chairman: W. D. HORNE.

Vice Chairman: F. W. ZERBAN.

Secretary: FREDERICK BATES.

Executive Committee: W. B. NEWKIRK, C. E. COATES, C. A. BROWNE, S. J. OSBORN, H. E. ZITKOWSKI, H. S. PAYNE.

FREDERICK BATES, *Secretary*

DIVISION OF WATER, SEWAGE, AND SANITATION

The varied and interesting program of the Division of Water, Sewage, and Sanitation was presented in full, each paper eliciting considerable comment. The paper, "Total and Available Calcium Hydroxide in Hydrated Lime," by A. S. Behrman and F. R. Porter, which introduced the special topic for discussion, namely, "Specifications for Lime for Water Treatment," was especially well received and developed a lively consideration of the whole subject of water softening. The report by Neave and Buswell, on the relative value of stirring *vs.* compressed air in the treatment of activated sludge, was of unusual interest and served as an introduction to a report, illustrated with photographs, by Dr. Bartow upon his observations during his recent European trip of the sewage treatment plants at Manchester, Sheffield, Bury, Strassburg, and Paris. An interesting report of some of the results of the inspection of commercial foreign and domestic waters, under the Federal Food and Drugs Act, was presented by Sale and Skinner.

The officers of the Division were reelected for the ensuing year.

W. W. SKINNER, *Secretary*

SECTION OF CHEMICAL EDUCATION

The Section of Chemical Education opened with an attendance of 241 at the first session. W. D. Bancroft, of Cornell University, presented the first paper on "Pandemic Chemistry." He stressed the great need for a course in chemistry intended for men who wish to learn something about the subject merely as a part of a general education, and briefly outlined such a course. He said that Cornell University is seriously considering starting a course on Pandemic Chemistry when the new laboratory is finished.

The next general topic of the "Correlation of High School and College Chemistry" was opened by L. W. Mattern, giving the high school standpoint, followed by another paper from the college's point of view by H. N. Holmes. Lyman C. Newell very keenly analyzed the entire forenoon's papers and discussions, and pointed out the difficulties that stand in the way of a proper correlation of high school and college chemistry. He believes that the two-course plan in college is the only fair one for students, and should be conducted when the class of beginners numbers 75 or more. Dr. Newell stated that the present basis of division into the two-course plan was not satisfactory, and suggested that teachers report at the New Haven meeting a new basis. It was voted that a committee of seven be appointed to study the proper correlation of high school and college chemistry and report their findings at the first meeting possible.

The discussion of the afternoon centered around the general topic, "What Chemistry Shall Be Taught in Our Professional Schools?" L. B. Broughton cited the chemical requirements for premedical students as specified by the American Medical Association. W. F. Rudd, in discussing dental chemistry,

touched upon the following points: first, the needs of freshmen students in chemistry in those dental schools requiring only high school graduation for matriculation; second, the needs in those schools requiring one year of college work for matriculation; third, the proper correlation of dental metallurgy and dental chemistry. J. C. Krantz described a method for the correlation of general and pharmaceutical chemistry, which received the applause of all present. C. W. Stoddart outlined an interesting course for agricultural chemistry which includes qualitative chemistry, agricultural chemistry including possibly organic chemistry and qualitative analysis, a separate course in organic chemistry, and a course in quantitative analysis which is closely allied with agricultural chemistry. C. W. Cuno discussed the present methods of teaching qualitative analysis as a preliminary to other courses in chemistry. Professors Gornoy and Bartow opened the Thursday morning program by a paper entitled "An Experience with the General Intelligence Tests in Teaching Freshman Chemistry." They showed how the general intelligence tests had a definite use in teaching freshmen chemistry, in spite of the fact that the marks of the student and the general intelligence ratings do not always have a close comparison. A motion was made and passed that a symposium on tests, including any standardizing test in chemistry, be held at the New Haven meeting.

A paper by B. T. Harvey, Jr., gave many helpful suggestions in meeting difficulties involved in teaching of chemistry in negro private schools. H. W. Moseley described a modified Hulett apparatus for the demonstration of the volumetric composition of water, and also a simple and effective ozonizer for lecture demonstration purposes. W. L. Estabrook gave a development of the Student's Laboratory Bench, including a demonstration of his apparatus. He also described two small wooden kits provided with shelves and capable of holding all the reagents, solids, and solutions needed in qualitative analysis, designed by L. J. Curtman of the College of the City of New York. R. A. Baker showed how the teaching of the electrochemical series might be of great aid in the teaching of chemistry. E. G. Mahin gave a clear idea of what he meant by the "Schoolmaster and the Teacher."

The Thursday afternoon session opened with Dr. Silverman acting as chairman. W. A. Noyes gave the first paper on "Proper Methods of Conducting Undergraduate Research." He said that if the instructor trained the student in proper methods of looking up chemical literature and developed personal initiative in the student, he had done much for the student's research career. R. E. Rose gave an extremely well worked out paper on "The Best College Course for the Chemist." His paper was such a radical departure from the course generally given to chemists that the Section did not seem to be ready to discuss it. This paper will undoubtedly be up for discussion at a later meeting when we will all have had time to read the article in full and think it through. J. B. Garner gave the last paper of the afternoon on "The Education of the Chemist." He showed in a very clear and convincing way that personality, mentality, and professional training are essential elements in the make-up of a chemist. Dr. Silverman made a motion that the Section of Chemical Education hold a joint meeting with the Division of Industrial and Engineering Chemistry, at which time there should be a symposium on industrial education. The motion was unanimously passed and the Milwaukee meeting was considered the best time for the symposium. The Section closed with the feeling that the next year holds much of value for all those interested in chemical education.

NEIL E. GORDON, *Secretary*

MEETING OF ASSISTANT EDITORS AND ABSTRACTORS OF CHEMICAL ABSTRACTS

The abstractors' dinner and meeting was well attended, over forty being present. It was held at the Pittsburgh Bureau of Mines Cafeteria. The feature was a talk by the former editor, Austin M. Patterson, who emphasized the point that the abstractors and editors should feel that their work on the journal is just as important and dignified as any work which they do in their laboratories. Just as in the business world the old feeling is disappearing that those engaged in distribution are on a lower plane than those who are producers, so also in the field of science the attitude that the distributors serve a less important purpose than the producers, is passing.

Dr. Edward Bartow, who has just returned from Europe, reported favorable comments across the sea on the work of the abstractors of *Chemical Abstracts*.

E. J. CRANE

SECTION OF GAS AND FUEL CHEMISTRY

The initial meeting of the Section of Gas and Fuel Chemistry was a symposium on combustion held jointly with the Division of Industrial and Engineering Chemistry under the chairmanship of R. T. Haslam. The importance of efficiency in using our fuel supply was emphasized by the chairman, who pointed out that \$2,500,000,000 per year is used at perhaps 10 per cent efficiency, so that even a small percentage increase in efficiency of combustion would represent a very great saving in dollars and cents.

Four of the papers in the symposium related to the physical-chemical principles underlying combustion reactions, developed from a semimathematical point of view. W. K. Lewis pointed out that the essential consideration is the burning of coke in the fuel bed where the velocity of various reactions occurring is of dominating importance. R. T. Haslam discussed two sets of reactions: (1) those occurring in simultaneous combustion of carbon monoxide and hydrogen; and (2) those in the production of water gas.

George F. Moulton reported on the extended investigations of that institution regarding domestic appliances designed for proper control of the combustion of gaseous fuels. A similar discussion of the problems involved in the burning of powdered coal was given from both a theoretical and practical point of view by Kreisinger and Blizard, who summarized the work done by the Bureau of Mines and the Combustion Engineering Corporation.

H. C. Dickinson described the important problems which demand consideration in a study of combustion in engine cylinders, pointing out the striking differences between reaction conditions there and in ordinary burners where gas or oil is burned at low pressure.

The final paper of the program was by J. A. Doyle on "Factors Governing the Selection of Fuels," with particular emphasis upon the importance of determining the cost per unit of the finished product, rather than simply theoretical efficiency or heating values.

Besides the symposium, 16 papers were presented at the meeting of this Section, and the large attendance and enthusiastic discussions prompted a vote of the Section requesting that the officers of the SOCIETY authorize a continuance of the session for the next general meeting. It is estimated that over 100 persons were present at the meetings of the Section, approximately 50 being in attendance continuously throughout the entire period.

The carbonization of coal was one of the most important general subjects considered. H. J. Rose described the new Becker coke oven, indicating the important increases in oven capacity which this new system of oven heating permits. The same author discussed the new electric method which has been developed for determining the by-product yields which can be expected from any coal.

A paper was given by H. J. Rose describing a system of impregnating the cut surface of a coke sample with a mixture of plaster of Paris and magnesia, in order to bring out the delicate detail of structure.

The methods of utilizing low-temperature cokes were discussed fully by H. A. Curtis, who described briefly the Carbocoal process for making low-temperature coke material which is then briquetted with pitch and made into a smokeless fuel which behaves much like anthracite and is entirely suitable for domestic use.

Physical-chemical studies of the forms of sulfur in coke indicate, according to A. R. Powell, that the sulfur exists both as a solid solution and as free sulfur physically adsorbed by the carbon, as well as in the form of ferrous sulfide.

The thermal efficiency of modern regenerative coke ovens was discussed by Wilson, Forrest, and Herty as a result of extended plant tests from which complete engineering data were obtained.

The constitution of coal and its relation to the storage of coal for combustion and the coking of coal was discussed in a series of five papers by S. W. Parr, T. E. Layng, and their associates in the University of Illinois. The same authors describe a method for determining the softening point of coal and the temperature at which the softened coal again solidifies as a coke.

Methods for the examination of low-temperature coal tars were reported on by J. J. Morgan and R. P. Soule. A paper by Weymouth, Anderson, and Fay described a new apparatus for determining specific gravity of gases in the field. The utilization of natural gas at low pressures for household work was discussed by Miss Anna P. Warren.

J. D. Davis described a new retort used for combustion of

coal samples to determine directly available hydrogen. R. T. Haslam and L. Harris discussed the making of fuel producer gas from powdered coal in order to achieve higher over-all efficiencies from fuel used.

R. S. McBRIDE, *Secretary*

SECTION OF HISTORY OF CHEMISTRY

Chairman C. A. Browne in his introductory remarks described the exhibit of books on alchemy, medical chemistry, metallurgy, and also the autograph letters and documents. This exhibit of books included Agricola's "De Re Metallica," Emanuel Swedenborg's "Regnum Subterraneum," Sir John Pettus' "Fodinae Regales" (1670) and "Fleta Minor" (1683), and Albaro Alonso Barba's "Minerals and Metallurgy" (1726). Dr. Browne stated that a movement was already on foot to prepare a large and elaborate historical exhibit for the New Haven meeting.

President Edgar F. Smith, in his paper on "James Curtiss Booth, Chemist," called attention to the fact that he was one of the early presidents of the AMERICAN CHEMICAL SOCIETY. After giving a short account of Booth's student life at the University of Pennsylvania, he described in detail Booth's studies with Wöhler and Magnus. Upon his return to Philadelphia, Booth organized a student chemical laboratory which eventually became the well-known firm of Booth, Garrett & Blair, Analytical Chemists. Booth also contributed several important reports to the geology of Pennsylvania and Delaware. In fact, he made the first geological survey of Pennsylvania. His greatest contribution to chemistry was made during his service as Director of the Mint in Philadelphia, which position he held until his death. In fact, his death was hastened by the arduous labor connected with the development of the processes of refining California gold. Besides these three contributions to education and science, Booth prepared many reports for the Franklin Institute, translated a French chemistry, Regnault's book on chemistry, and also wrote an encyclopedia of chemistry.

In his second paper, President Smith gave a vivid account of the chemical work of Richard Watson, the Bishop of Llandaff, and exhibited his portrait and autographed letter and a volume of his essays. John A. Mathews described in detail the development of iron-making in the colonies from the first iron made from iron ore in Jamestown in 1608 until just after the American Revolution. In his paper on "Some Relations of Early Chemistry in America to Medicine," Dr. Browne described the work of John Winthrop, Jr., George Stockey, and William Beaumont. F. B. Dains, in "The Early History of Some Experiments in General Chemistry," showed that many of the experiments performed are really very old. The cartoons of van't Hoff shown by Ralph H. McKee epitomized the career of van't Hoff in a pleasing manner. Elton R. Darling pointed out that bromine was produced in Pennsylvania and other states many years ago and the flourishing industry was established long before the present one in Michigan. Lyman C. Newell's letters of Davy emphasized the striking characteristics of the famous English chemist, and the two diplomas signed by Dalton brought vividly to the audience the contributions of this English chemist to the atomic theory. The unpublished letter of Berzelius interpreted by Anton R. Rose revealed the versatility of the great Swedish chemist.

The officers of the Section were reappointed and are making arrangements for the New Haven meeting.

LYMAN C. NEWELL, *Secretary*

SECTION OF PETROLEUM CHEMISTRY

The meeting of the Petroleum Section, the fourth since its organization at Rochester, was marked by a large attendance, the steady interest of technologists prominent and influential in the petroleum industry, and a noticeable awakening of attention from chemists identified with the theoretical, rather than the applied science. A great deal of interest attached to the activities of the Section in promoting research on petroleum, and the matter was discussed thoroughly. The committee appointed at Birmingham to select a list of problems for immediate attack and to cooperate with the Research Division of the American Petroleum Institute reported, and was instructed to consider at once means for starting work on the research problems on a cooperative basis. It is hoped that, besides the direct benefit resulting from the solution of the problems attacked, this activity of the Section will result in awakening the interest of chemists generally in the field of petroleum chemistry.

The program included some fourteen papers of general interest, a symposium on "Lubrication from the Chemists' Viewpoint," and a discussion on the origin of petroleum. The latter consisted of formal papers by R. E. Somers and R. Thiessen, and discussion by C. F. Mabery and W. H. Emig. The papers in the lubrication symposium covered the chemical composition of lubricants, the mathematical aspects of lubrication, and some practical questions. Unfortunately, several of these papers remained unread because of the absence of the authors. There was much open discussion.

The change from the sectional to the divisional form of organization was authorized at this meeting. The officers elected under this authority were:

Chairman: T. G. DELBRIDGE.

Vice Chairman: R. R. MATTHEWS.

Secretary: W. A. GRUSE.

Executive Committee: E. W. DEAN, W. F. FARAGHER.

W. A. GRUSE, *Secretary*

CHAIRMEN AND SECRETARIES GROUP

About 35 chairmen and secretaries met at three o'clock Thursday afternoon. In the absence of W. Lee Lewis, E. C. Franklin of Leland Stanford University presided.

Since the term of office of Professor Lewis had expired, it was in order to elect a presiding officer for the coming year. Professor Lewis was unanimously reelected.

The Secretary read a letter of Professor Lewis relative to the activities of the group. The results of the questionnaires sent to the different Sections were reported. After discussing both sides of the question whether or not it would be advisable to ask the national officers to give this group the status of "Section" it was unanimously voted to make this request.

Much valuable discussion took place with regard to the best method of securing members for the SOCIETY, how to get members acquainted, and how to get local publicity. The itinerary of the speaking tour of E. C. Franklin was laid out. The following Sections are planning to have him speak before their members at the time he comes east for the spring meeting at New Haven: Chicago, Detroit, East Lansing, University of Michigan, Purdue, Cleveland, New Orleans, West Virginia, Pittsburgh, Buffalo, Rochester, Syracuse, and Philadelphia. It is hoped that other Sections will also attempt to have Dr. Franklin on their programs while he is on his way to the meeting.

Dr. Miner of the Chicago Section told of a typical program before the Chicago Section. The meeting was divided into four parts, and at the close of the discussions before these groups the members came together and enjoyed sandwiches and a social time.

It was suggested that the Chairmen and Secretaries Group get together for an informal discussion at each national meeting, owing to the decided change in personnel, and also to the fact that different sections of the country were visited.

It was also pointed out that much interest was stimulated in Sections by holding joint meetings with their neighbors, and it was planned to have at least one intersectional meeting a year. This brings about good fellowship and gives the younger men in the Sections a chance to present papers and become acquainted with the leaders in the chemical profession.

ERLE M. BILLINGS, *Secretary*

American Ceramic Society—Summer Excursion Meeting, August 13 to 19, 1922

This meeting was purely an excursion. There were no literary or executive sessions held, the entire occasion being devoted to plant inspection and to meeting with the several people in the different localities.

The trip down the St. Lawrence to Montreal is well worth the while of any one who desires to observe scenery, architecture, or human nature. One could not possibly talk shop on such a trip.

The reception accorded by the officials of the potteries and glass companies in Montreal was most cordial. They entertained the seventy-five guests Monday evening with a smoker, and on Tuesday night with a banquet.

Tuesday was filled with plant and city visitations. The McGill University with its several laboratories and museums was visited by practically every delegate. The Montreal potteries, glass companies, brick works, and enameling works entertained them royally.

On Wednesday the party journeyed to Buckingham to visit the feldspar mines of O'Brien and Fowler. They were met in Buckingham by automobiles for a ten-mile ride into the wilds. Here they saw the quarrying of feldspar under the most modern conditions and by the most modern methods. A wonderful camp dinner was served and the delegates were entertained with singing by local talent.

From Buckingham the party continued in special cars to Ottawa, where a banquet was served and the Victoria National Museum and the Department of Mines were visited.

On Thursday afternoon the party divided into groups and visited different ceramic plants, paper mills, and other points of interest in the city.

The party left the city at 10:40 for Verona, where again they were royally received and entertained, and motored up into the mountains to the Richardson feldspar deposit, after which they continued their journey to Kingston where they were received by the Kingston Council.

The cordial reception given, the banquets served, the addresses made by distinguished Canadians repaid the delegates for the time and expense of the trip. Words cannot express the appreciation of the wonderful service rendered by the Canadian Pacific Railway. The party had the same parlor cars and porters from Montreal around to Kingston, and the continuous service thus afforded made the trip easy. After the banquet Thursday night in Kingston, the party took special sleepers for Toronto, finding that while they were at the banquet their bags had been conveyed from the special parlor cars to the sleepers by representatives of the Canadian Pacific Railway. This is typical of the sort of service that Canada gave the American delegates.

At Toronto the party was received with the same cordiality, and the day's stay was planned with the same detail and expedited in the same fashion as on the other days. In Toronto and on the next day in Hamilton the party saw more of the works that were branches of American companies. Sanitary works, glass works of all sorts, brick and tile companies, universities and museums afforded a wide variety of interesting and instructive things to be seen.

The American Ceramic Society would fail in its real purpose if it did not afford its members these opportunities for excursions, not only to see ceramic plants, but to see the best that nature affords in lakes, rivers, mountains, etc., and also the best products of human effort, not only in the universities, museums, wonderful cities, but also in mankind. This trip on Lake Ontario, down the St. Lawrence, and up into the Canadian mountains, completely encircling Lake Ontario cannot be surpassed in the large variety and quality of things to be seen, entertainment furnished and in opportunities for studying and observing manufacturing. [ROSS C. PURDY, *General Secretary*.]

Meeting of Chemical Equipment Association

The Chemical Equipment Association, at its final organization meeting on September 2, 1922, at which 32 active and 4 associate members were present, elected the following officers:

President: Pierce D. Schenck, Duriron Co.

Vice Presidents: Walter A. Lummis, Adolph Coors, Jr., Coors Co., George J. Lehman, Bethlehem Foundry Co.

Treasurer: P. C. Kingsbury, General Ceramics Co.

Directors: H. N. Spicer, Dorr Co.; J. I. Lyle, Carrier Co.; P. S. Barnes, Pfauder Co.; Edw. C. Alford, Shriver Co.; T. C. Oliver, Chemical Construction Co.; H. H. Alport, E. B. Badger Co.

This association was organized on May 10, 1922, for the purpose of fostering trade in chemical process equipment. The aims of this association are given on page 564 of the June issue of THIS JOURNAL.

Chemical Salesmen Meet

The Salesmen's Association of the American Chemical Industry, in executive session at the Hotel Commodore, New York, on September 12, 1922, elected the following officers for the next year:

President: John W. Boyer, The Mathieson Alkali Works, Inc.

Vice Presidents: F. M. Fargo, Jr., Calco Chemical Co.; Edward Van Berlo, Wilckes-Martin-Wilckes Co.; Edgar M. Queeny, Monsanto Chemical Works.

Secretaries: J. D. Lowery, Kalbfleisch Corp.; George T. Short, Wilckes-Martin-Wilckes Co.

Executive Committee: Williams Haynes, Drug & Chemical Markets; R. T. Dunning, The Barrett Co.; W. S. Goff, Monsanto Chemical Works.

NOTES AND CORRESPONDENCE

A Criticism of the Technical Press

Editor of the Journal of Industrial and Engineering Chemistry:

A shortcoming of the chemical press of to-day is the lack of forceful, constructive criticism of the profession. The technical journals ably expound to the layman the value, achievements, and necessity of chemical control and research in industry, and in this we must admit they do a great service to the chemist. But this is only a part of their duty. They should clearly and persistently point out to the chemist his own weaknesses and the pitfalls that surround him. To trust this self-analysis to the individual chemist is asking too much of human nature. We are none of us prone to search out our faults, but it is wholesome and necessary that they be pointed out to us.

You have in your JOURNAL an interesting and valuable department—"The Earning Power of Research." I would suggest another department under some such title as "Business Mistakes of Chemists," frankly devoted to picking apart and criticizing the activities of the average chemist in industry, which should have a cumulative effect in maintaining high standards of effectiveness in the profession.

Another duty of the technical magazine is education. The average chemist is unaware that his education is incomplete in the details of business. The chemical laboratory, whether research or testing, presents in miniature all the administrative and executive problems of the industrial plant. Its raw materials are reagents and chemicals, its finished product, service or information. All the industrial problems are met here, whether the force consists of two or thirty—buying, storage and control of raw materials, securing, training, and development of competent workers, upkeep of equipment, maintenance of quality, and quantity of production. The problems of merchandizing also enter in. Is the product of the highest attainable quality, and does it meet in an adequate way the customer's special needs (the "customer" being of course the firm, department, or man making use of the results)? Is it properly presented and explained? Viewed in this light, the operation of a laboratory at its greatest efficiency for commercial purposes, requires, besides mastery of the principles and technic of the science involved, application of the basic principles of economics and psychology, business instinct, and attention to business detail. Chemists do not study and apply as extensively as they might the excellent works available in efficiency and business management. It would be to their advantage to do so, for the man who really can, and knows he can, make every dollar invested produce the maximum result in any line of endeavor is never without a job. Further, he is the type of man most justified in going into business for himself. The technical magazine should call attention to books on these subjects, publish articles dealing with the application of sound economic principles to the chemist's daily work, and investigate and endorse, or even institute, if necessary, suitable correspondence courses for instruction in these subjects.

The technical journal can render a further service in the cultivation of morale. The chemist is perhaps a little too ready to bewail his lot when things do not suit him, and instead of being discouraged in this attitude by the technical press, he is led to feel that his services are not appreciated. Granting some basis of truth in this, it is surely not a healthy viewpoint to adopt, nor one that can lead to real progress. The technical journal can be of assistance here by trying to inculcate a forward-looking viewpoint which makes light of difficulties and brings success in its wake. This is no time for the chemist to pine. The pres-

ent era of close competition, which will probably last for a period of years, is his golden opportunity to prove his worth as a money saver and money maker. But, like everyone else, he must be prepared to work harder than before.

The captious may comment that seemingly all that is further necessary to bring the technical journal up to date is the adoption of a pretty-girl cover, a woman's page, and a bed-time story, but I sincerely believe that the chemist in industry will look more and more to the technical press for guidance and inspiration as well as for technical information. The time is past when a mere bound file of proceedings and technical reports and papers will fully serve his needs.

I believe that a technical journal working strongly along these or similar lines would in a few years exert an enormous influence for the better on the morale, efficiency, and prosperity of the chemical profession.

HUGO V. HANSEN

45 NORTH SPRING ST.
BLOOMFIELD, N. J.
June 15, 1922

The Continuous Countercurrent Lixiviation of Charred Kelp

Editor of the Journal of Industrial and Engineering Chemistry:

The article on "The Continuous Countercurrent Lixiviation of Charred Kelp," by J. W. Turrentine and P. S. Shoaff, in THIS JOURNAL, 14 (1921), 605, offers excellent opportunity for application of the theory of discontinuous extraction developed in THIS JOURNAL, 9 (1917), 866. The data given in the article, together with other figures on the water content in the filter cakes—kindly furnished by the authors—make it possible to compare the ratio of KCl to water in the solutions with those in the corresponding filter cakes. In Filter Cake 1 the ratio of KCl to water was 37.6 to 100, while in Brine 1, supposed to have been in equilibrium with the filter cake, the ratio was only 30.2 to 100, showing that there was some undissolved KCl in the first filter cake, or, what is just as bad, the solution remaining in the cake was of higher concentration than that removed by filtration. In the same way it was found that the ratio of KCl to water in Filter Cake 2 was 10.6 to 100 and in Brine 2, 10 to 100, showing that the solution was not quite complete even after the second treatment. By the theory of discontinuous extraction, undissolved solute after the first treatment decreases the efficiency of the process, and this process could, therefore, have been improved by better mixing or higher temperature in Agitator 1.

This note is not offered as adverse criticism of Turrentine's process, but simply as an example of a method of studying discontinuous extraction processes to determine where improvement can be made. In this particular process the solvent ratios are so high and the general efficiency so good that these considerable quantities of KCl undissolved after the first treatment probably do not affect the recovery by more than a few tenths of a per cent, but in many processes such undissolved solute might seriously decrease the recoveries.

It would be inadvisable to finish this note without explaining why a discontinuous extraction theory is applied to a process called continuous. The explanation is that the process is really a typical discontinuous, countercurrent extraction, but instead

of taking the space to prove this assertion we will leave it as a problem for those of your readers who are interested in the theory of extraction. Here is a paradox. In an extraction process the raw materials enter and the finished products leave the system continuously, and all the intermediate products are constantly in motion, and yet the process is *discontinuous*, countercurrent extraction.

L. F. HAWLEY, *In Charge*
Section of Derived Products

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN
July 27, 1922

Editor of the Journal of Industrial and Engineering Chemistry:

With reference to the communication of Dr. L. F. Hawley, permit me to say that when a process in which the raw materials are being added continuously, the intermediate products are in motion continuously, the extraction up to the point where equilibrium exists between solid and solvent takes place continuously, the finished products are discharged continuously, and which is in practical operation continuously, is yet *discontinuous*, it might be contended that the definition is more open to criticism than the process.

J. W. TURRENTINE

EXPERIMENTAL KELP POTASH PLANT
SUMMERLAND, CALIFORNIA

Larger Quantities of Creatine Available

Editor of the Journal of Industrial and Engineering Chemistry:

It should interest biological and pharmaceutical chemists to learn that creatine, heretofore obtainable only in gram lots at a price of several dollars a gram, is now available in much larger quantities. A source of this material has been discovered which, while not unlimited, is capable of yielding at least some hundreds of pounds of pure creatine a year.

In order that research workers may be able to benefit by this discovery, a considerable quantity of pure creatine has been prepared, and will shortly be available through regular supply houses at a fraction of one per cent of its present price.

It is hoped that this new source of creatine may aid materially in extending our knowledge of this and related substances, as the quantity now available should permit research in this field along the lines of nutrition, pharmacy, and synthetic organic chemistry, as well as biochemistry, without exorbitant expense.

The writer will be glad to give further details to anyone interested.

GRAHAM EDGAR

UNIVERSITY OF VIRGINIA
UNIVERSITY, VA.
August 25, 1922

Correction

On page 745 of the August issue of THIS JOURNAL, change the heading "Society of Chemical Industry Reports" to read "Chemical Society (London) Reports." Also make the following change in the first line of the text: Delete the words "Society of Chemical Industry" and substitute "Chemical Society (London)," making that portion of the sentence read: "The Council of the Chemical Society (London) is prepared to offer, etc."

Chemists Storm the Capitol

Editor of the Journal of Industrial and Engineering Chemistry:

On August 16, 1922, twenty-six research, operating, and analytical chemists,¹ representing sixteen different synthetic organic chemical plants, mustered up courage enough to present without other support their side of the embargo question to the arbiters of the tariff at Washington. "A horde" Senator Moses called us on the floor of the Senate. I presume, however, we should be grateful for even that public recognition—it is one of the few that chemists, as such, have had.

Sunday, August 13, the outlook for the embargo seemed particularly black. Since its failure would mean to the country the irreparable loss of the industry and to us the equally serious loss of our jobs, Messrs. Orelup, Schepmoes, and myself, in discussing the matter on that day, concluded that we had little to lose and everything to gain by organizing a group of men similarly situated to present the chemists' side of the organic chemical tariff in Washington.

The time was too short for long explanations, but we felt certain the cause was so good that but few men would be unwilling to risk the relatively small cost of the trip in the hope of doing something to save their industry and positions. All honor to those men who joined us, but we were sadly discouraged in a great number of cases. Some who would not join us felt that the chemists would not know enough about the situation to be effective, or would be ignored. Fancy! After long years of arduous training and an average of several years of practical experience, we are still uncertain of our abilities to meet men and present our ideas! As for being ignored, it is a rare public representative indeed that desires to avoid his constituency, much less dares to!

As a matter of fact, we had not only an interesting and instructive visit, but we most certainly aided in the accomplishment of our ends. Senator Frelinghuysen graciously aided us in arranging interviews with the President, Secretary Hoover, and with the other members of the Senate Finance Committee. We interviewed Senators Edge, McCumber, McLean, Watson, Calder, Lenroot, Sterling, Shortridge, Capper, Fletcher, Shepard, Nicholson, McCormick, and Borah, and quite evidently influenced several former embargo opponents in favor of the Bursum Amendment then pending.

At least partly as a result of our plea, Senator Ransdell not only voted for the Bursum Amendment but also made a speech in favor of it. Probably the most interesting result of our visit was the outcome of our long talk with Senator Borah, who promised a vote in favor of an embargo to be long enough to reestablish the industry, if our contention proved true—that two months of the then tariff (without the Bursum Amendment) would put us out of business.

One thing our visit made plain—that legislation is accomplished by far different means than research along chemical lines. From our talk with one senator it was quite plain that uncorrected misstatements had been made on the floor about our industry, and that the actual situation was little appreciated except among those already favorable to the measure. It was obvious that, not only was it not undesirable for such a party of individuals to press its case, but that it would be absolutely fatal not to, for without "lobbying" of a sort proper legislation could not be obtained.

Finally, I hope that some of your readers will send to the *Con-*

¹ The members of the party were: A. P. Beardsley, James Brown, E. E. Hartmann, J. J. Johnson, P. V. Rosenvelt, H. A. Van Brocklin, L. L. Perry, J. W. Orelup, F. A. Novotny, R. W. Feder, C. H. Schepmoes, W. W. Weck, William Goldstein, W. A. Lucas, L. M. Shafer, N. R. Viera, C. Hamilton Merrill, R. E. B. Richards, C. A. Swan, E. G. Parker, A. C. Winttingham, W. H. Van Winkle, M. T. Coakley, T. B. Clendenning, and L. C. Ohlsson.

gressional Record Office, The Capitol, Washington, for copies (at about 10 cents each) of that very interesting publication of August 17 and 18, where on pages 12,537 and 12,576 will be found the debate on the Bursum Amendment. Let them not fail to read the words of Senator Moses on page 12,542: "I suppose, Mr. President, the way to become a chemist in this country is to put a label in your lapel." Then let them ponder how far the chemist in this country has yet to go to find his place in the sun, and how much personal effort each must put forth to do it.

A. J. PASTENE

CHEMICAL COMPANY OF AMERICA
SPRINGFIELD, N. J.
August 25, 1922

Canadian Letter

By T. Lindsay Crossley

208 KING ST., WEST, TORONTO, CANADA

Canadian industries using heavy chemicals are buying in larger quantities, and while this business has not by a large margin reached the volume hoped for, the improvement in the last five months has been marked.

Canada seems to be popular as a summer meeting place. These visitors are not only welcome, but they are an inspiration to good fellowship. Last month we had the Chemical Engineers and the Leather Chemists. Ere this appears, the American Ceramic Society will have been with us, and the American Electrochemical Society will visit Montreal and Shawinigan, September 21 to 23.

They will see one of our best examples of industrial development in the St. Maurice Valley, due to the magnificent water powers of the St. Maurice River at Shawinigan and Grand Mere, developing about 225,000 h. p. at both places, with a third power of about the same amount, not developed, at Les Gres below Shawinigan. Grand Mere is a pulp, paper, and power town controlled by the Laurentide Company. Shawinigan has pulp and paper mills, carbide, electrometallurgical and aluminium works, foundry, cotton mills, and technical school. Here was developed the biological process for acetic acid, and here were made special aluminium alloys for aeroplane construction, and the first commercial magnesium in America.

The Canadian Institute of Chemistry is planning an active program for the fall and winter, and is rapidly becoming a factor in the scientific development of the country.

It is said that one reason for the lack of public attention to the work of chemists is that chemists themselves do not cooperate and are not found mingling with the folks in the market place. With a view to meeting this criticism in some small measure, the chemists of Toronto have inaugurated an informal luncheon club, meeting every Monday at the Engineers' Club, where questions of general interest are discussed and from time to time action by various organizations may be suggested. This has already been found of practical value.

Some discussion has been aroused by a proposal made during the Ottawa convention to adopt the word "chemor" as applying to consulting, analytical, or engineering chemists, to avoid the confusion arising from the idea, perhaps more prevalent in British communities, that chemist is synonymous with retail druggist. In fact, some provincial legislation in Canada makes the pharmacist the only person legally defined as a *chemist*. Hence the suggested new appellation to bring the distinction to public notice.

August 2, 1922

The Plant Manager and the Chemist

Editor of the Journal of Industrial and Engineering Chemistry:

I cannot allow Mr. George L. O'Brien's criticisms of the chemist in *THIS JOURNAL*, 14 (1922), 650, to pass unanswered.

Chemists, like other people, are neither perfect nor infallible and their ideas are not always practicable, neither are those of any manager I have known.

Mr. O'Brien would make of the chemist the "catalytic agent" or go-between of about everything that transpires in the plant and community, yet without authority. If it were possible to fill such a position, I can scarcely see what occasion there would be for a manager. A man of such parts would be discredited for holding a subordinate position.

It is as important for a manager to know management as it is for a chemist to know chemistry. Believe me, I have seen some managers who were out of place. Chemists, with slight exceptions, are conscientious workers, but in the business of management I have seen many examples of a betrayal of trust.

Often there has been, and is yet, a lack of cooperation between the management and the chemist. The manager does not know how to make the best use of his chemist and he is often suspicious of the man who has new and original ideas. The time is rapidly approaching when the chemical industry will be managed by chemical engineers, as it should be.

I have one important criticism to make of the manager. Generally speaking, he expects to pay a chemist a clerk's salary, and too often, I regret to say, he gets away with it because the chemist is willing to take a position which he is led to believe promises a "future." A chemist is always at a disadvantage in looking for a position. It is not a popular profession and not many chemists are wanted.

Chemistry lies at the foundation of all life and being, and its pursuit requires special natural qualifications, consistent, hard, and conscientious endeavor. The chemist is not above criticism but he should be dealt with in a kindly sympathetic spirit of encouragement. Mr. O'Brien concludes his criticism with a very high compliment to the chemist when he says, "much of the progress of civilization rests with him," and that, "his activities are of such great importance that modern industrial manufacture without his help is unthinkable."

MARTIN L. GRIFFIN, *Chemist*

MT. HOPE FINISHING COMPANY
NORTH DIGHTON, MASS.
July 29, 1922

Figures Talk

The registration, by states, of those present at the Pittsburgh meeting of the A. C. S. was as follows:

Alabama	1	Maine	3	Oregon	1
Arkansas	2	Maryland	30	Pennsylvania	582
California	4	Massachusetts	47	Rhode Island	1
Colorado	3	Michigan	25	Tennessee	2
Connecticut	14	Minnesota	10	Texas	4
Delaware	16	Mississippi	3	Utah	1
District of Columbia	62	Missouri	11	Vermont	2
Georgia	2	Nebraska	2	Virginia	10
Illinois	69	New Hampshire	2	Washington	2
Indiana	20	New Jersey	38	West Virginia	21
Iowa	11	New Mexico	1	Wisconsin	25
Kansas	5	New York	150	Canada	6
Kentucky	2	North Dakota	1	England	2
Louisiana	7	Ohio	159	Cuba	2
		Oklahoma	1		

TOTAL REGISTRATION 1362

Studies of the effects of sulfides on animals are being made at the Bureau of Mines Experiment Station, Pittsburgh, Pa., by a number of consulting physiologists, including Yandell Henderson, Howard W. Haggard, C. W. Mitchell, and W. P. Yant.

LONDON LETTER

By HUGH GRIFFITHS, 15 New Bridge St., London, E. C. 4, England

CRYSTALLIZING PLANTS

Considerable interest is now being taken in this country in the modern types of apparatus for crystallization in motion; a number of firms having installed new plants during the past few months. In view of the recent decision under the Key Industries Bill in connection with sodium hyposulfite, it is probable that much more attention will have to be paid to the form and appearance of commercial chemicals. Sodium hyposulfite of "photographic quality" is now scheduled, and while it was clearly stated by the Referee that "pea-crystal hypo" may not be of "photographic quality," the latter term is taken to indicate a product of good color and high purity in the form of small uniform crystals.

While this may be considered a clear definition, it will be recognized that most photographers have their own ideas as to what photographic quality "hypo" looks like, and usually they will expect to receive either the "cube crystal" or "pea-crystal" form. Like many other users of chemicals, they do not usually make an analysis of materials but judge of their suitability from appearance. The photographer's experience has led him to associate satisfactory performance with a certain appearance, and it is therefore necessary for the manufacturer to meet his ideas.

The same considerations apply to every chemical product to some extent, and it is safe to say that a crystalline substance of regular appearance consisting of individual grains of uniform size and shape is generally more readily salable than the less beautiful ordinary qualities. This is not necessarily the result of fact, but is because the user has learned that a carefully crystallized material will generally be better in other respects also.

A large number of inorganic substances are now sold in regular crystalline form, all these having the same essential features, namely, the crystals being approximately of pea size or larger, and the crystals being quite separate and not formed in groups, and each being of nearly perfect shape and of uniform size.

The production of these qualities on a large scale is generally only possible in special plants, only the fine grain materials being produced in ordinary agitator-crystallizers and stationary vessels yielding agglomerated masses of crystals.

At present, two types of plant are being used: a simple open plant, and a more elaborate vacuum apparatus. The open plant consists essentially of a long trough of approximately elliptical section which is oscillated on roller bearings by means of gearing. This trough has no jacket, the cooling being for the most part due to the evaporation of water from the exposed liquor. These machines are generally between 30 and 80 ft. in length.

The solution to be crystallized is run into this trough at one end, and the small crystals which are at first formed gradually increase in size as they pass on a zigzag path through the apparatus; the finished crystals together with the mother liquor are discharged at the other end and received on suitable draining apparatus. The motion of the crystals in the trough prevents agglomeration, and if the correct physical conditions are chosen, most inorganic commercial salts can be turned out from these simple machines in the form of regular individuals of even size. Quite apart from any question of appearance and quality of products, these machines are proving attractive on account of the continuity of operation and economy of labor.

Some modifications have been introduced into these plants recently in order to secure better control over the crystal size, but details are not yet available for publication.

The vacuum crystallizers are also of the oscillating type, and consist of cylindrical boilers supported on rollers, the various connections being made through hollow trunnion packings. These may be of any size, and while they are more elaborate than the open crystallizers, their application appears to be more generally possible and the crystals may be produced in very large sizes. The writer has some samples of cane sugar crystallized in these machines, and the crystals are about $1\frac{1}{2}$ in. across, weigh about 1 oz. each, and are perfectly shaped and separate individuals just like crystallographic models.

It is to be expected that the study of the operation of these plants will lead to a better knowledge of the *rationale* of crystallization. Most chemists find it difficult to believe that large crystals can be obtained from a moving liquor, but it is now well established that if the other conditions are correct and the for-

mation of too many new centers of crystallization can be avoided, perfect crystals can only be produced from a liquid in motion. The convection currents in ordinary stationary crystallizers seem to have been forgotten.

The two types of plant mentioned above are now in use on many different materials: sodium sulfate, sulfite, thiosulfate, sulfide, phosphate, nitrate, carbonate, alums, chlorate, bichromate, copper sulfate, sugar, organic acids, etc.

NITRIC ACID MANUFACTURE

The latest volume of the "Technical Records of Explosives Supply," on the manufacture of nitric acid from nitrate of soda, gives a fairly accurate account of the present state of English practice.

While silica-coil condensation systems are favored in many quarters, the preponderance of technical opinion is certainly in favor of the Hart plant, in which condensation is effected mainly in glass tubes about $1\frac{1}{4}$ in. diameter. As in America, the systems employing submerged condensers are not recommended, owing to the serious consequences of a leakage of water into the condenser—namely, the dilution of an entire batch of acid, which is expensive to concentrate.

The speeds of distillation given in the report are for war practice, and under ordinary conditions most works are content to make two runs from each plant per 24 hrs., and with gas-fired retorts this speed can be maintained comfortably while securing a very high over-all efficiency.

The use of silicon-iron condensing plants is not common in England, owing to the difficulty in obtaining really sound castings in such alloys. Some years before the war a system very similar to that described in the August issue was given a very thorough trial, the only essential difference being that the S-pipes were of flattened section. Such systems have been tried repeatedly since that time, but invariably they have been given up, owing to the difficulty experienced in getting pipes free from blow-holes and graphite pockets. Some of the makers of acid-resisting castings are now adding a small proportion of nickel with a view to securing a finer grained metal, and are also taking steps to produce clean sound castings. One manufacturer has succeeded in producing straight tubes in this metal by the centrifugal process, and the solution to the difficulty may be found in this method. There is, of course, no question that, given really good castings, the silicon-iron condenser would be far better than any ceramic production.

The report gives some particulars of an interesting attempt to construct a continuously working plant for reconcentration of nitric acid, by running the mixture of nitric and sulfuric acids through a packed tower heated externally by producer gas. Several continuous systems for this concentration have been tried in England, but none of them have been found to be so satisfactory as the simple distillation process, repair charges generally proving to be excessive.

METHYL BROMIDE

While ethyl chloride, methyl chloride, and ethyl bromide are all inflammable, it has been pointed out by Albert Henning that methyl bromide is not only noninflammable but a very powerful fire extinguisher, and patents have been taken out to cover application of this material as a solvent, as a refrigerating agent, and also as a fire extinguisher.

It is specially interesting as a fire extinguisher, as, by reason of its low boiling point, 4° C., it does not require mechanical devices for projection, the vapor pressure being adequate to propel the bromide from a suitable container fitted with a simple nozzle. Such extinguishers have been demonstrated on several occasions recently, and it has also been shown that petrol is rendered noninflammable by admixture with about one-fifth the proportion of methyl bromide as compared with carbon tetrachloride. This is not surprising in view of the vapor pressures of these materials. It is also claimed that there is less danger of poisoning than with tetrachloride.

For refrigerating purposes both methyl bromide and mixtures of methyl bromide and ethyl chloride are now in use in place of ethyl chloride in the small size machines. The fire risk, which has always been the most serious objection to these machines, is therefore eliminated.

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

THE DYE INDUSTRY

The syndicate of dyestuff consumers has taken the initiative in asking for customs regulations to protect this industry, but limiting this protection to dyes made in France. The dyestuffs not yet made in French factories would be almost entirely free from duty.

This measure seems to be rather tardy, for the production of dyes in France is increasing daily. The French importation of dyes before the war reached 95 per cent of the national consumption. In 1920 the amount of imports was not more than 60 per cent; in 1921 and at the beginning of 1922 it decreased to 20 per cent. In 1920, 50 per cent of the amount imported came from Germany (3000 out of 6000 tons); in 1921 the importation was only 400 tons, coming from Germany.

This decrease of importation is due largely to the efforts of the National Company of Dyestuffs and Chemical Products. I mentioned previously the rumor concerning the union of this company with the German companies. This rumor has been, and is still, contradicted. Nevertheless, the dye company has bought a number of patents from the foreigners. It certainly does not wish to lose time in perfecting the manufacture of intermediate products; it has resolutely acquired all the manufacturing processes that it has been able to find concerning these products.

The procedure of selling dyestuffs by chemical engineers specializing in dyestuffs is being developed in France. This method of selling the manufactured products has been successful; it gives satisfaction to weavers and dyers by permitting collaboration with technical color chemists. These technicians have themselves made the chemicals in special laboratories where the uses of coloring materials are studied.

MEASUREMENT OF WEAK RADIOACTIVITIES

The electroscopes now used for measuring weak radioactivities are all derived, more or less, from the electroscope of Curie and Laborde. Mr. Szilard has proposed a spiral electroscope. The needle is movable and the index rigid, and is electrically joined to the case. It is attracted by an insulated dial and charged by a very small electric friction machine. The needle is suspended by a fine ribbon stretched so that the torsion will be an antagonistic couple.

With such an electroscope, Mr. Szilard has been able to measure on 500 g. of a product containing 10^{-9} of radium per gram. One division of his apparatus corresponds to 10^{-4} electrostatic units, which is to say a content of 0.001 U_3O_8 . This apparatus seems destined to render great service in the measurement of weak radioactivity control of manufacture in radium factories, prospecting of minerals, examination of fertilizers and medicines with weak radioactivity.

THE NITROGEN PROBLEM

The French Parliament was dismissed before making a decision on this question. This is especially unfortunate, as we are still in a period of discussion between the two processes—Haber and Claude. It is a national fault of ours to spend much time in discussions after making an interesting discovery, so that we are too late to put it into use.

Mr. Matignon at Marseilles gave us information as to the nitrogen situation in Germany. In this country there has been a slight increase in price of nitrogen products, due to an increase in cost of transportation.

In spite of last year's catastrophe, the factory at Oppau has since February 1922 returned to its normal production, which is 100,000 tons of pure nitrogen per year. The factories at Leuna are producing 200,000 tons per year. The dividends issued by the different societies of chemical industries (Hoechst, Badische, etc.) have increased about one-third.

Furthermore, Germany has made herself completely independent of the nitrates from Chile, of which she received 750,000 tons before the war. She imported from Chile in 1921 only 35,000 tons of nitrates, which have been replaced by calcium nitrate. The Bavarian factories are furnishing 80,000 tons of this per year, the Saxony plants, 175,000 tons. These plants use the Franck-Caro process.

By summing up the different quantities of nitrogen produced in Germany—both as nitrates and as ammonia—it can be seen that at the present time Germany produces about three times as much as it can consume for its agricultural needs. With a low rate of exchange it can rapidly become an exporter of this product, while we in France are still in a period of discussion.

Our investigators, however, are continuing their study of the different phases of the problem, and Mr. Sabatier has just specified the conditions of obtaining urea directly from carbonic acid and ammonia. On the other hand, Mr. Matignon has also fixed the conditions of obtaining ammonium sulfate directly by treating calcium sulfate (gypsum) with ammonium carbonate. At ordinary temperatures by agitation for 2 or 3 hrs. with gypsum a concentrated solution of ammonium carbonate changes into a solution of ammonium sulfate. This conversion is almost total, as the coefficient of conversion is 96 per cent.

INTERNATIONAL COUNCIL OF RESEARCH

The International Council of Research has just convened at Brussels. Around this International Council are now grouped five great international Unions: Astronomy, Geodesy and Geophysics, Mathematics, Scientific Radiotelegraphy, Pure and Applied Chemistry. Only the Union of Pure and Applied Chemistry meets annually.

Four new Unions have been established: Pure and Applied Physics, Biological Sciences, Medical Sciences, Geography.

The decline of the German mark has made possible at the Stassfurt mines a large exportation of their potash, and just as the Dyestuffs Company has had to form an alliance with the German societies, the companies mining Alsatian potash have had to seek an alliance with the German producers. Preliminary arrangements have been under way since May. They have been difficult to bring about, but they seem now to be nearly completed.

The impossibility of bringing about payment by Germany is going to cause more and more French industries to seek special alliances with industries on the other side of the Rhine. It is well understood that these alliances are purely economic and not political, and that they leave to the French industry all complete freedom of action.

The English society, British Dyestuffs Corporation, has in the last few years undergone great financial difficulties. The factories which it has erected, constructed hastily, perhaps with insufficient technical preparation, have not been able to furnish the same quality of dyestuffs as those furnished by the German or Swiss concerns. The English customers, have, therefore, finally returned to these old suppliers. In spite of the tariff duties protecting the British Dyestuffs Corporation, this society was in danger and engaged in conferences with the president of the syndicate of German producers of dyestuffs. No agreement was made, because of the fact that the English society did not succeed in making acceptable to the German representatives the principle of absolute autonomy of the English dyestuffs industry corresponding to the needs of peace time as well as to those of war. The French Dyestuff Company has been able to come to the agreement of which I have spoken. Now, in France, we only import 15 per cent of our total consumption of dyestuffs.

The International Congress of Geology has just been held at Brussels. One of the questions which they have been discussing with much breadth is that of sources of petroleum. A specialist in this matter, Mr. Voitești, of the University of Cluj (Roumania) has examined the sources of petroleum in the Transylvanian region. Mr. Bogdanovitch showed the parallelism of bituminous and petroleum deposits with the richness in phosphates of neighboring rocks. The author came to this conclusion following the discovery of bituminous and phosphate schist in the state of Montana, U. S. A.

From October 9 to 15 there will take place in Paris the International Congress of Combustible Liquids, presided over by Prof. Sabatier, a member of the Institute. This Congress is divided into six sections: (1) Petroleum, (2) Schists, (3) Coals and Peats, (4) Tars and Benzol, (5) Alcohols, and (6) Vegetable Oils.



JAPAN LETTER

By K. KASHIMA, 1125 Ikebukuro, near Tokyo, Japan

The fixation of atmospheric nitrogen is an important problem in European countries and also in Japan. Under the jurisdiction of the Agricultural and Commercial Department, an institute, Special Research Laboratory for Nitrogen, was established in 1917 at Meguro, near Tokyo, to study this problem and its application to industry. Dr. Fusakichi Odera, formerly research chemist of the Tokyo Industrial Laboratory, was placed in charge of the laboratory. Details of the progress of the institute have not yet been published. Three reports have, however, appeared: concentration of nitric acid using sulfuric acid as a condensing agent; a general review of the fixation of atmospheric nitrogen; and the electrolysis of cyanamide, its salts, and dicyandiamide in aqueous solutions.

The same problem is now under consideration by the Institute of Chemical and Physical Research, and also by some fertilizer companies. Two companies were founded by the Mitsui and Mitsubishi, with plants in Kyushu, and employ the cyanamide process. Suzuki and Company, in Kobe, have recently purchased the apparatus and patent for the fixation of nitrogen from Georges Claude of France. This apparatus is also protected by the Japanese patent law. Founded on this and other patents, the Nitrogenous Industrial Company of the Claude System is being organized with a capital of 15,000,000 yen to manufacture ammonia, ammonium sulfate, and other derivatives.

The fuel situation is another international problem. Recently, two institutes have been established to study this question: The Research Laboratory of the Naval Fuel Department at Tokuyama in Yamaguchi Prefecture; and the Fuel Laboratory, of which Mr. Manji Yoshimura is in charge. The latter, which is under the control of the Agricultural and Commercial Department, will study general fuel problems and their industrial application. The former, under the Naval Department, will conduct research work on fuels for ships.

During the past year, Tatsuzo Hatori of Minami-hirayangi-nura, near Kawaguchi-machi in Saitama Prefecture, made the startling announcement that by heating certain common substances in a crucible with suitable reagents, he had succeeded in isolating some small silver grains. These substances did not reveal the presence of silver by the methods ordinarily employed. His announcement aroused the interest of chemists, many of whom called upon him and examined his work. But they could not explain his findings. Some thought them fantastic. The inventor himself has not been able to offer a scientific explanation. He is not a college man but is a trained technician. Dr. Tsuneya Marusawa, professor of applied chemistry in the Kyushu Imperial University, and Dr. Sadahiko Sato are greatly interested in his work and are conducting investigations with a view to finding the scientific explanation for this discovery. Dr. Sato has recently announced that he can isolate silver from some substances which do not yield silver by the usual analytical method, but has not yet advanced a scientific explanation.

July 15, 1922

Books and journals published in the United States and European countries are frequently bound with metallic wires. They are not, however, suitable for Japan, owing to the great humidity. Japan is a wet country, the humidity being at a minimum in January, about 60 per cent, and at a maximum in July, about 90 per cent. Metallic wires used for binding books and journals, leathers used for covering cameras and other purposes, and many wooden articles are apt to be destroyed during June to August.

Many patents for waterproof paper or cloth have been taken out. Prof. K. Ikeda has perfected a process for the manufacture of drying agents. As material, Japanese acid clay (fuller's earth) was selected, which is being largely used as decolorizing material of mineral, vegetable, and animal oils. The clay is compressed to a prism 10 to 15 mm. long and a sectional area of about 4 sq. mm., and heated to a high temperature. By passing moist air or other gases through a layer of the prism, it is easily dried. By the decrease of 1 mm. of the vapor tension, the temperature of the gas is raised by 2°. When the absorbing power of the clay is lost, it is reactivated by heating or by passing heated air.

A. Maire, chief engineer of St. Médard powder-mill, has visited this country and is now delivering lectures on chemistry and technology concerning explosives, etc. The visit of American chemists is very much welcomed. It would be a great pleasure if we could hear their opinions directly. It has already been announced that Prof. Einstein will visit this country next autumn and deliver some lectures on his great theory. If visitors drop into our laboratory, every assistance in our power will be gladly offered.

Research is the life of scientific men in the laboratory, but it consumes money. The funds for research in universities, technical and other schools are not plenty. For a few years, the Educational Department has been granting some money (about 1000 to 3000 yen per problem) to scientific men in universities, technical, higher, or medical schools, etc. This year, about 30 professors were appointed for such research. Works achieved by this fund are now being published in general chemical journals or special memoirs of each school.

There have been three chemical journals written by Japanese—*Journal of the Chemical Society of Japan*, formerly *Journal of the Tokyo Chemical Society*, founded in 1880, *Journal of Chemical Industry*, founded in 1898, and *Journal of the Pharmaceutical Society of Japan*, founded in 1882. This year two new chemical journals have been published, *Acta Phytochimica*, edited by Prof. K. Shibata, and *The Journal of Biochemistry*, edited by Prof. S. Kakiuchi. They contain articles written in English, French, and German.

The National Research Council of Japan has also published this year one proceedings and eight journals—on astronomy and geophysics, chemistry, physics, geology and geography, botany, zoölogy, medical science, and engineering. They contain transactions written in English, French, and German, and abstracts written in English of articles published in Japan. Besides these, we have one chemical news (semimonthly), two rather popular chemical journals, and many special publications from institutes, colleges, or laboratories.

An institute for studying metallic materials was newly established in the Tôhoku Imperial University in Sendai instead of the Iron and Steel Laboratory, Prof. K. Honda being appointed as the director of the Institute. A chair for biochemistry has been established in the Kyoto Imperial University and is held by Prof. S. Komatsu. It will also be created in the Tokyo Imperial University in the near future.

August 11, 1922

A Uniform Working Temperature

For some time the need for uniform alcohol tables and a uniform temperature for making routine observations has been felt. There has been some criticism of the two standards now in most common use, that of the A. O. A. C., which is based on the Bureau of Standards table 20°/4°, and that of the U. S. P., based on the Bureau of Standards tables 15.56°/15.56°. In order to obtain a consensus of opinion as to preferences, the following questionnaire was recently sent out to members of the A. O. A. C.:

- 1—Are you in favor of the A. O. A. C. alcohol tables?
- 2—Are you in favor of the U. S. P., 9th Revision, alcohol tables?
- 3—What single working temperature do you consider best for determining specific gravities, optical readings, refractive indices, immersion refractometer readings, etc.?

Of the replies received, the vast majority voting favor the A. O. A. C. tables, and 20° as the best temperature for making determinations.

In order to get a larger and more representative vote, it has been suggested that others, who are interested in establishing uniform tables and temperature for making observations, send their vote on the three questions, especially on the question of uniform, general working temperature. The preferences of the members of the AMERICAN CHEMICAL SOCIETY are especially desired in this matter. Suggestions should be sent to L. F. Kebler, Chairman, A. O. A. C. Committee on Pharmacopoeial Revision, Bureau of Chemistry, Washington, D. C.

WASHINGTON NOTES

DYE SITUATION

On August 17, 1922, just about a month after the dye embargo was defeated by a vote of 32 to 38, the Senate, by vote of 38 to 23, adopted the Bursum Amendment, which increased the duty on coal-tar intermediates from 50 per cent ad valorem and 7 cents per lb. foreign valuation to 75 per cent ad valorem and 10½ cents per lb. American valuation. It also increased the duty on coal-tar chemicals and dyes from 60 per cent ad valorem and 7 cents per lb. foreign valuation to 90 per cent ad valorem and 10½ cents per lb. American valuation. It further empowered the President, after thorough investigation, to make certain reductions in these schedules.

When the conferees reached this item in their consideration of the Tariff Bill, they rejected the Bursum Amendment and substituted the dye embargo. Then the House took its turn and, after an acrid debate of several hours, by a vote of 177 to 130, recommitted the bill to the conferees with instructions to abandon the embargo and to place potash on the free list. It is believed that it was this linking of the dye embargo with potash that caused the defeat of both in the House. The conferees agreed to the action taken in the House, but with the proviso that the new rates adopted should be based upon American valuation.

And now, as we go to press, another step has been taken toward the restoration of the dye embargo. On September 16, Senator Wadsworth introduced a Joint Resolution in the Senate, providing that the embargo be extended for four months after the passage of the Tariff Bill. On the following day Representative Tilson introduced a similar resolution in the House, except that under the terms of the House Resolution the embargo is to be retained for three months instead of four. Coincident with this action, Secretary Mellon called attention to the difficulty that will be experienced by customs officials in determining American values, and suggested that time be allowed these officers to determine the American values on dyes imported into this country.

The dye industry is having a hard fight, but it seems incredible that a way will not be found to insure the adequate protection of this industry.

HELIUM PLANT REOPENED

A large plant for the extraction of helium from natural gas has been reopened at Fort Worth, Texas. The appropriations made by Congress for this work are sufficient to permit the plant to operate for practically the entire year. It is under the general supervision of the Navy and is operated by the Linde Company under a government contract. The plant has been shut down since November 1, 1921.

DYE PRODUCTION IN 1921

A report of the United States Tariff Commission states that on account of the loss of export trade, business depression, and large stocks on hand, the dye production in this country showed a marked decline as compared with the previous year. However, notwithstanding poor business conditions, a considerable number of complex dyes were developed and introduced during the year. Many of these dyes are essential to special processes of dyeing and printing, although the quantity consumed makes them of secondary importance from that standpoint. The development of these new products is a notable technical achievement and represents further progress toward rounding out our coal-tar chemical industry.

There were 201 firms manufacturing coal-tar derivatives in 1921. The output of dyes by 74 of these firms was something more than 39,000,000 lbs., representing a decrease of 56 per cent from the 1920 production. The sales during the same period were more than 47,000,000 lbs., with a value exceeding \$39,000,000. Sales exceeded production by 22 per cent, indicating clearly the presence of large stocks carried over from the previous year's abnormally high production. The sales for 1921 exceeded the imports of 1914, when nearly 46,000,000 lbs. were imported and 6,000,000 lbs. of dyes made from German imported intermediates.

It is worth noting that the average price of all dyes in 1921 was 83 cents per lb., compared with a value of \$1.08 per lb. in 1920 and \$1.26 for 1917. The importations were 3,914,036 lbs. valued at \$1.32 per lb., making a total of \$5,155,779, compared with \$5,763,437 for 3,402,582 lbs. the previous year. Of the dyes im-

ported, Germany supplied about 48 per cent, Switzerland 41 per cent, England 7 per cent, and other countries 4 per cent.

Exports of American dyes for 1921 decreased nearly 79 per cent as compared with 1920. They were less than for the year 1917 when the vast expansion of domestic dye industries from those of pre-war times occurred.

The development of the synthetic organic chemical industry has been similar to that of the dye industry, and the production of medicinals, perfumes, flavoring ingredients, and solvents is 21,545,186 lbs.

GOVERNMENT EMPLOYEES

The following statistics taken from data issued by the Civil Service Commission show the changes in the number of government employees which are wholly or principally the result of the World War:

	Employees in District of Columbia June 30, 1922	Employees Out- side District of Columbia June 30, 1922
State	595	3,257
Treasury	19,860	36,110
War	4,921	46,358
Navy	7,377	48,470
Labor	1,161	2,364
Shipping Board ¹	1,888	2,182
Railroad Administration	1,123	124
Alien Property Custodian	139
Supt., State, W. & N. Bldgs.	1,006
Veterans' Bureau	5,321	26,481
Railroad Labor Board	75
Civil Service Commission	379	30
TOTALS	43,770	165,451

¹ Include administrative offices of Emergency Fleet Corporation, but not workmen at yards or employees in warehouses or on vessels.

SUMMARY

NUMBER OF EMPLOYEES	In District of Columbia	Outside District of Columbia	TOTAL
June 30, 1916	39,442	398,615	438,057
June 30, 1922	69,980	490,883	560,863
INCREASE, ENTIRE SERVICE	30,538	92,268	122,806

THE SURGEON GENERAL DESIRES COÖPERATION ON THE PART OF INDUSTRY

As part of a comprehensive study under the direction of the Assistant Secretary of War, the Medical Department of the Army is undertaking a study of the sources from which the supplies which it uses can be obtained. The Medical Department is not only concerned with the provision of the personnel necessary to the treatment of the sick, but is also charged with the supply of those things that are required by such personnel.

The armamentarium of modern medicine is exceedingly intricate, but without it the wonderful advances made in medicine are not available to the sick and injured, however skilful the personnel. The difficulties encountered in providing such elaborate equipment in time of war for the large number of new hospitals, infirmaries and first aid stations necessary, and particularly in providing it at these institutions in the advance area, are manifest, and yet, if the soldier is to be given the service that he is entitled to, it must be provided.

In a war of any magnitude the burden thrown upon industry for the production of these supplies is enormous. Any information that could be made available in advance to industry as to type, number, and quality, would obviously be of great advantage to industry in its plans. The Surgeon General, therefore, side by side with his plans for the extension of the Officers' Reserve Corps, with his plans for instructing medical students through the R. O. T. C. in those duties of a medical officer which differ from those of the civilian physician, is determining where the supplies needed by these officers may be had, should any grave emergency arise.

This effort is an attempt to do beforehand what was necessary after the declaration of war in the recent World War. It is in recognition of the fact that the forces of the Medical Department, however numerous and skilful they may be, will be but half prepared without the necessary equipment. In brief, the program contemplates: (1) That a careful determination shall be made, not only of the items needed, but of the quantity thereof. If a close liaison with industry is established, it is probable that final decision as to the type of an article selected will be determined

often by the facilities of industry to produce it in large quantity; (2) the plan contemplates also a roster of personnel skilled in the manufacture, and the inspection and purchase of the various commodity groups. It is desired to secure from industry itself men who are eligible and will accept reserve corps commissions with a view to their assignment in time of emergency to the procurement of the commodity in which they are specialists. It is purposed that upon these men reliance will be placed in time of peace for advice and assistance in the study of industrial facilities, and that in time of war they will be assigned to the centers of industry or to Washington for procurement duty; (3) the plan further contemplates that a thorough study be made of the facilities of the country to produce the essential and important items of the supply table, and to have on file in the office of the Surgeon General such reports as will enable the immediate placing of contracts in the event of any national emergency.

In this work the Surgeon General realizes that he must rely upon industry itself, and it is hoped to secure definite and complete information from the manufacturers as to the aid they can render. It is probable that in an emergency of any magnitude Congress would again establish control of raw materials, labor, transportation, and installations; and the medical department expects that, with such information on file, it will be in a position to render great assistance to the firms making medical depart-

ment supplies. It can prevent the drafting of skilled labor, the taking of key men, can assure the supply of material, of coal, and of transportation, and thus obviate difficulties in the operation of the plant.

At the direction of Secretary Fall of the Interior Department, T. E. Swigart, petroleum technologist, and C. E. Beecher, oil recovery engineer, of the Bureau of Mines, have been designated to compile a handbook of conservation methods in petroleum production, to be used by operators on leased public lands. The manual will include discussions of sources of wastes in oil and gas fields; suggested methods of preventing wastes in the production of oil and gas; and a complete, revised set of rules, regulations, and penalties for violation of regulations as applied to oil and gas production on public lands of the United States.

The Carbohydrate Laboratory of the Bureau of Chemistry has developed a cheap, effective, and rapid process for preparing chocolate creams having very soft cream centers. Invertase, instead of an acid, has been used to secure the semiliquefaction of the centers, the flavor developed being superior to that ordinarily secured by other methods. Application has been made for a public service patent to cover this process.

September 18, 1922

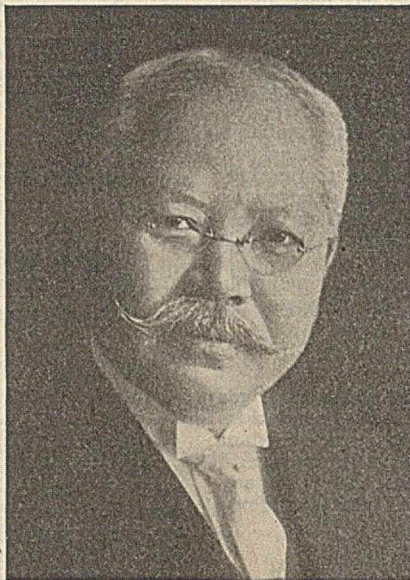
OBITUARY

Dr. Jokichi Takamine

ONLY to a few men is the opportunity given to act as so strong a link between two nations as was Jokichi Takamine, who died in Lenox Hill Hospital, New York, N. Y., on July 22, 1922, at the age of 67, after an illness of many months. His earnest desire for lasting friendship and good understanding between his native land of Japan and his adopted home of America was continually evidenced in his manifold activities.

Dr. Takamine was born November 3, 1854, in Takaoka, Japan, his father being physician to the Prince of Kaga. At the age of twelve he was sent to Nagasaki to study under the tutelage of the Portuguese consul, and later went to Osaka to study medicine. He became more interested in chemistry than in medicine, and entering the Imperial University at Tokyo graduated as a chemical engineer in 1879. The government then sent him to Great Britain for three years' special study in the University of Glasgow and Andersonian University. Upon his return to Japan he was appointed chief chemist of the Department of Agriculture and Commerce. His work in this capacity did much to improve the brewing industry of Japan and led to his lifelong activity in the scientific investigation and commercial development of diastatic ferments. In 1884 he came as representative of the Japanese government to the Cotton Centennial Exposition at New Orleans. Here he met Miss Caroline Hitch, whom he married in 1885. He planned to make his home in the United States, but returned to Tokyo in 1887 to erect there the first superphosphate plant in Japan. In 1890, he again came to America, and not long thereafter, as the result of his researches upon diastatic ferments, organized the Takamine Ferment Company in Chicago. These same researches resulted in the development of Takadiastase for medicinal use.

In 1900 his isolation of crystallized adrenalin as the active principle of the suprarenal glands brought to a climax a long series of researches by various eminent men, and made its commercial production possible. It is in this connection that the



JOKICHI TAKAMINE

name of Takamine is most widely known.

He was instrumental in the establishment in Japan of numerous chemical industries, including the production of alkali, aluminum, fertilizers, and dyes, and also formed there a large pharmaceutical corporation, Sankyo and Company.

In recognition of his accomplishments the University of Tokyo in 1899 bestowed on him the degree of Doctor of Chemical Engineering, and in 1906 that of Doctor of Pharmacology. His ability was so highly esteemed by his native country that in 1913 the Emperor appointed him a member of the Royal Academy of Science and in 1915 decorated him with the Fourth Order of the Rising Sun.

Dr. Takamine's industrial interests were many, including the presidency of Sankyo and Company of Tokyo, the Takamine Ferment Co., the International Takamine Ferment Co., and Takamine Laboratories, Inc. He was also a consulting chemist for Parke, Davis and Company.

His scientific and social relationships were equally numerous. He was a member of the American Chemical Society, The Chemical Society of England, the Institute of Chemical Engineers, and the Franklin Institute, as well as one of the founders of The Chemical and Physical Research Society of Japan. Besides holding membership in many New York clubs, he was chiefly instrumental in founding the Nippon Club of New York and the Japan-America Society, and was among the founders of the Japan Club and the Japanese Association of New York.

Those who knew him personally will remember him best for his kindness, his thoughtfulness of others, and his intense devotion to every duty he deemed to be his.

His industrial ability achieved commercial success for himself and others; his scientific attainments brought him deserved honors; but a no less important contribution to the world's welfare was the years of quiet and persistent endeavor to promote enduring friendship between two great peoples; to interpret to each other the nations of his birth and his adoption.

FRANK O. TAYLOR

Personals

Mr. Robert I. Wray and Mr. Fulton B. Flick have accepted positions in the Research Bureau of the Aluminum Company of America, New Kensington, Pa.

Mr. John W. Crombie is now research associate at the American Sheet & Tin Plate Research Laboratory, Pittsburgh, Pa.

Mr. Donald E. Cable has resigned as assistant research chemist in the Agricultural Experiment Station of the University of Wyoming and has been awarded a university fellowship in chemical engineering at Columbia University.

On July 31, Dr. H. D. Gibbs resigned his connection as research chemist with E. I. du Pont de Nemours & Co., Wilmington, Del., and will take a much-needed vacation. For the present his address will be c/o Chemists' Club, New York, N. Y., or c/o Cosmos Club, Washington, D. C.

On July 1, A. A. Holmes resigned from the staff of E. B. Badger & Sons Co., Boston, Mass., to accept the sales management for the Trona Corporation. His headquarters will be in the Woolworth Building, New York, N. Y.

Dr. James Kendall has been promoted to a full professorship at Columbia University. He is to begin his sabbatical leave of absence next February, and has arranged to divide his time between Stanford University and the University of California.

Mr. H. Gardner McKerrow, who for the past three years has been advertising manager for the National Aniline & Chemical Co., Inc., has resigned and will engage in business in New York, as an advertising and merchandizing consultant, specializing in textile and chemical matters.

Mr. M. B. Crowe has severed his connections with the Crown Oil & Refining Company and has accepted a position in the Acid Recovery Department of the United Lead Co., Houston, Texas.

Mr. Ulric J. Lebourveau, Stamford, Conn., has resigned from the Atlas Powder Co., where he was engaged in experimental development work.

Dr. Gerald L. Wendt resigned on July 1 as associate professor of chemistry at the University of Chicago to join the staff of the Standard Oil Company of Indiana in the direction of research.

Mr. Leslie H. Webb, vice president of the Wedge Mechanical Furnace Co., is now in charge of the Pittsburgh office of the Pennsylvania Salt Mfg. Co., of which the Wedge Company is a subsidiary.

At a recent meeting the State Board of Regents changed the form of administration of the graduate work of the University of North Dakota from that of a department in charge of a graduate committee to that of a graduate school, and Dr. G. A. Abbott, head of the chemistry department, was appointed dean of the graduate school.

Dr. H. C. Trimble, associate professor of organic and physiological chemistry in the University of North Dakota, has been granted leave of absence in order to pursue special studies with Dr. Folin of Harvard.

Mr. Washington Platt has resigned his position as production manager of the Harris Laboratories to become associated with the Merrell-Soule Sales Corporation of Syracuse, N. Y., as manager of the Technical Service Department.

Mr. F. W. Barker, Jr., has resigned from the National Aniline & Chemical Co., Inc., and has become associated with The Kaumagraph Co., New York, N. Y.

Prof. Robert E. Wilson has left the Massachusetts Institute of Technology, where he was director of the Research Laboratory of Applied Chemistry, to assume direction of research for the Standard Oil Company at Whiting, Indiana.

Dr. J. A. LeClerc has severed his connections as chief chemist with the Miner-Hillard Milling Company and has assumed his duties as Special Agent in the Department of Commerce, Washington, D. C.

Dr. T. T. Read, chief of the Information Service of the U. S. Bureau of Mines, was appointed official representative of the American Institute of Mining and Metallurgical Engineers to attend the International Congress of Engineering held in Rio de Janeiro, Brazil, in September.

The Trustees of Columbia University have granted Victor K. LaMer, instructor in chemistry, leave of absence for the year 1922-23 to accept the Wm. Bayard Cutting Traveling Fellowship. Dr. LaMer sailed about September 15 for England and Denmark, where he will continue his studies in physical chemistry.

Industrials

On July 26, 1922, the new laboratories of the Research Association of British Rubber & Tire Manufacturers at Croyden, England, were formally opened. The association was formed in 1919 for the study of the fundamental problems of the rubber industry, the preparation of information dealing with control of manufacturing operations, the testing of raw materials and final products for practical use, the collection of rubber literature, the adjudication of scientific disputes, and the coördination of scientific and technical work in national emergencies. Some practical work in the study of physical and chemical problems has been carried on in laboratories at University College, London, but with the opening of the new laboratories it is expected that the full program will soon be put into execution.

As a direct result of the amalgamation of the General Bakelite Co., the Condensite Company of America, and the Redmanol Chemical Products Co., the Electroplax Company has been established at Toronto. The company is being financed entirely by Canadian money, and will produce the cold molded products and the various industrial articles now made by all the companies in the United States. The officers of the new company are: president and general manager, H. E. Corey; vice president, L. V. Redman; manager, W. M. Davidson; factory superintendent, J. B. Rathbun; chemist, W. A. Campbell.

Celite Products Limited has been established in Canada to market Sil-O-Cel and Filter-Cel as produced by the Celite Company in the United States. Sil-O-Cel is used for the prevention of excessive heat loss from boilers, furnaces, etc., while Filter-Cel is used in filtering to secure greater clarity and brilliance of filtrate. Mr. Lawrence Russel has been appointed Canadian manager, with offices in the New Birks Building, Montreal.

Brotherton & Company Ltd., Leeds, England, have published a booklet entitled "Hydros" which gives in some detail the method employed by them in the quantitative determination of sodium hydrosulfite.

Jayne & Sidebottom, Inc., New York City, have been appointed by the Darco Sales Corporation as sole selling agents in the New York metropolitan district and New Jersey for Darco decolorizing carbons.

The Salt Lake Insecticide Co., Salt Lake, Utah, has begun work on its plant for manufacturing calcium arsenate from the Scorodite ore found in the Gold Hill district, Utah. The arsenic ore is said to be high grade and is located in a hill of limestone-garnetiferous. Dr. Frank K. Cameron discovered the process by which the ore can be economically treated and manufactured into calcium arsenate, and will act as general manager of the plant.

The Westmoreland Chemical & Color Co., Philadelphia, Pa., has had its plant closed as a public nuisance by order of the director of the Health Department. For several years there have been complaints that the escape of sulfuric acid fumes has caused considerable damage to property and the health of the residents in that section of the city, but until recently the company has been able to have definite action deferred on the plea that it was working on a special washer that would enable it to recover the acid. The present order requires that the plant shall remain closed until a system shall have been installed that will effectually prevent the escape of the acid fumes.

The Cellulose Products Co., incorporated under the laws of Delaware for the purpose of manufacturing artificial straw and hair, is to have a modern brick and steel factory building erected for it by the Chamber of Commerce of Milford, Del. It is said that this plant will be the first of its kind in America.

The following statistics are given relative to the exports from and imports into the United States of dyes during June 1922:

	Exports	Lbs.
VEGETABLE DYE EXTRACTS		
Logwood extract.....		366,871
Other dye extracts.....		286,854
COAL-TAR COLORS, ETC.		
Color lakes.....		282
Other colors, dyes, and stains.....		398,975
	Imports	Lbs.
Alizarin and alizarin dyes.....		74,887
Colors or dyes.....		292,676
Indigo, synthetic.....		8,310
Extracts and decoctions for dyeing.....		323,239

BOOK REVIEWS

Der Betriebs-Chemiker. Ein Hilfsbuch für die Praxis des Chemischen Fabrikbetriebes. By DR. RICHARD DIERBACH, Fabrikdirektor, and DR. ING. BRUNO WAESER, Chemiker. 3rd edition. x + 334 pp., 117 illustrations. Julius Springer, Berlin, 1921.

An examination of this excellent publication awakens a sense of the need for a similar handbook in English, adapted to conditions prevailing in industrial chemical plants on this continent. This is exactly the book for the young chemist or chemical engineer finding his place in the operating organization of a chemical industry for the first time. It gives a vast fund of detailed information concerning those important details which most textbooks sublimely ignore. The availability of such a book in English would undoubtedly eliminate the asking of many questions, and would prevent many foolish mistakes in setting up chemical plant of all kinds.

The book is conveniently divided into sections, the first of which constitutes the bulk of the book. This section is divided into chapters on materials of construction, piping, valves, meters, furnaces, boilers, engines and electrical power transmission, material handling, and pumping equipment. The second section deals with the location and construction of buildings; the third, with the functions of the industrial chemist, and the maintenance of laboratories; the fourth, with safety engineering; and the fifth is a sort of symposium of short papers on various manufacturing operations, grinding, mixing, evaporating, distilling, drying, etc. Unfortunately, the authors have felt it necessary to limit themselves to very few pages on each of these subjects, and the information given is hardly full enough to be of any real help and the material is probably included here merely for the sake of completeness. The sixth section gives a very brief treatment of by-products; the seventh deals with chemical plant accounting, but merely skims the surface of this involved subject; and the eighth deals with packing and shipping.

The book is well printed and the illustrations are excellent. The binding, however, is not particularly well adapted to the hard service which such a book must receive.

F. M. TURNER, JR.

Power Alcohol: Its Production and Utilization. By G. W. MONIER-WILLIAMS, O.B.E., M.C., M.A., PH.D. 323 pp. Henry Froude and Hodder & Stoughton, London, 1922. Price, 21s. net.

This book appears at a time when it is most needed. Alcohol will unquestionably be one of the ingredients of the future motor fuel. The author should be commended for his efforts to help at this critical time and congratulated on his able presentation of the subject.

The motor fuel problem is clearly defined in the first chapter; more stress should be laid, however, on the possible development of the steam engine for motor purposes.

Three-fifths of the book is given over to the manufacture of alcohol. This is as it should be. The chapters on fermentation are clear, though technical. Perhaps a better appreciation of the conditions in the United States and of the importance of molasses would improve the treatise as an international text. The addition of more engineering detail would have increased the value of the book. This is especially true of the chapter on distillation.

Dr. Monier-Williams has analyzed the situation without stating his personal conclusions, leaving the reader to form his own

opinions which could be done more quickly if the author had summarized his data.

The remaining two-fifths of the book deals with denaturation, the internal combustion engine, properties of alcohol, fuel tests, and fuel mixtures. The importance of the denaturant is well brought out. The chapters on the internal combustion engine, and on properties of alcohol, are concise and clearly stated. The chapter covering motor fuel tests is an excellent review of the reliable work that has been done, but a one-page summary of the results would aid the reader in obtaining a clearer perspective. The final chapter describing fuel mixtures deserves more space because of its present interest.

The author states that alcohol is not going to become immediately a competitor of gasoline but a mixture containing alcohol will soon become a substitute for gasoline. He does not state, however, that gasoline must be one of the components of this mixture, an opinion that is held by many.

"Power Alcohol" is of particular importance to the English reader, but the American will find it both interesting and valuable.

D. B. KEYES

Kolloide Lösungen. By JOACHIM LEIMDÖRFER. 107 pp. Verlag für Chem. Industrie, H. Ziolkowsky, G. m. b. H. Augsburg, Germany, 1921. Price, M. 65 +.

The author, who is well known for his work on soaps, takes great pains to give colloids their proper perspective and his book (whose preface dated August 1914 indicates a long delay in its publication) possesses a somewhat philosophical character.

Starting with three essentials: (1) material movable particles (matter); (2) motion (energy); and (3) space, he points out that the three ideal states of the aggregation of matter—gas, liquid and solid—may coexist. From the work of von Weimarn and O. Lehmann, the author concludes that aggregation is the consequence of the vectorial orientation of matter, and he terms "crystal atoms" small material units whose sizes run between those of atoms and those of biological cells, and whose combination may yield macroscopic crystals or develop to cellular size.

Condensing matter gives off energy to the surrounding "solvent," and may yield coarse mechanical subdivisions, colloidal dispersions, or chemical combinations. In true solutions the forces are balanced, but colloidal solutions, possessing residual potential energy, are labile. Chemical combinations are broadly distinguished from dispersions in that the units involved are of a definite size, which persists under fixed conditions.

The book is deficient in experimental matter, but gives a general review of the subject based mainly on the work of Thomas Graham, Wo. Ostwald, P. P. von Weimarn, and others. During the seven years that the manuscript lay dormant, great strides have been made, and it will be interesting to see how the author will react in a new edition, when he becomes acquainted with the more recent work of American and British physicists and chemists, *i. e.*, of Thompson, Rutherford, Aston and Moseley, W. C. McC. Lewis, H. R. Procter and J. A. Wilson, of Milliken, Langmuir, Harkins, and G. N. Lewis, of T. W. Richards, J. Loeb, M. H. Fischer, and many others. His views will also be modified by the results of Scherrer at Göttingen with Bragg's X-ray spectrometer, which showed that colloidal solutions (*i. e.*, of SiO_2 and SnO_2) may contain both crystalline and amorphous or haphazard molecular clusters, whereas gelatin showed no crystalline groups.

JEROME ALEXANDER

The Manufacture of Pulp and Paper by the Joint Committee on Vocational Education. Vol. 3. Joint Committee on Vocational Education representing the Pulp and Paper Industry of the United States and Canada. McGraw-Hill Book Co., Inc., New York, 1922. Price, \$5.00.

This volume by nine experienced men contains a very full account of this subject to date, and the appliances and processes are very well illustrated. In general, the authors have not been as conscious of their audiences (students) as they should have been. Descriptive matter has been given more prominence than underlying principles, through which alone progress is made. There is considerable overlapping and repetition.

Somewhere in the complete book a discussion of the power plant, water supply, and transportation in the manufacturing processes should have been covered. As a work of reference a more complete bibliography should have been included.

The book commends itself as the product of practical men rather than book-makers. The committee and the associations they represent deserve only praise for undertaking such a task designed to enlighten all those connected with the manufacture of pulp and paper in order to keep it in the front ranks of industry.

MARTIN L. GRIFFIN

The Chemistry of the Non-benzenoid Hydrocarbons and Their Simple Derivatives. By BENJAMIN T. BROOKS. 612 pp. The Chemical Catalog Company, Inc., New York, 1922. Price, \$7.00.

This volume is chiefly a compilation of detailed information regarding a wide range of hydrocarbons and derivatives not included in what is usually referred to as the benzene series. Much of the material presented is not found in the generally available textbooks of organic chemistry, and for this reason the book will undoubtedly be appreciated by chemists who lack the time or facilities to review original literature. It promises, also, to serve as a convenient bibliography of hydrocarbon chemistry.

The volume represents a tremendous amount of work, but it is obvious that the author has devoted more effort to the collection of his material than to the method of presenting it. The reviewer recognizes the impossibility of developing an absolutely satisfactory classification of all the types of compounds discussed, but believes, nevertheless, that it would be possible to effect considerable improvements in the arrangement employed in the present work.

The typographic make-up of the book could undoubtedly be improved, and a more judicious selection and systematic use of titles and sub-titles would be advantageous. Several instances of misspelling, probably due to insufficient care in proof-reading, have been noted.

E. W. DEAN

Women in Chemistry. *A Study of Professional Opportunities.* 272 pp. Bureau of Vocational Information, 2 West 43rd St., New York, N. Y. Price, postpaid, paper bound, \$1.10; cloth bound, \$1.60.

This guide to the opportunities for woman in the various fields of chemistry will be of great help to those who are trying to decide upon a vocation. Too often the momentous choice is made by chance. It may be determined at the critical moment by a temporary liking for a particular study, by the influence of a teacher, by the example of a friend, by a casual newspaper item, or by the mere drift of circumstance. The sensible way of settling the question is to study the industry, its requirements and opportunities, its present pay and future prospects, and then to appraise frankly one's own capabilities and disposition for the situations attainable. But it is not human nature to proceed in such a rational manner in such important matters, and

moreover the necessary data in regard to the conditions and openings in any given industry have not hitherto been made available. That excuse for ill-considered choice of vocation is now being removed by the Bureau of Vocational Information in such volumes as the present.

There are some 20,000 professional chemists in the United States and about a thousand of these are women. It is therefore a limited field but offers a new and congenial career to educated women. Those who have the genius for original research will find a free field in most institutions. For able and well-qualified women to teach chemistry there is a great demand, especially in connection with home economics. Women are doing well in analytical work in hospitals, industries, and government laboratories.

This volume discusses each of these fields and others, giving frankly its advantages and disadvantages, and telling what qualifications and training are needed and where the training can be obtained. Our readers will be interested in what Dr. Ruth Clark, a psychologist, finds to be the qualities most needed for success in the field of chemistry:

- 1—Mechanical ability and skill above the average.
- 2—A logical mind.
- 3—Enjoyment in solving concrete detail problems.
- 4—Physical health and endurance above the average.
- 5—Ability to work independently without supervision.
- 6—Ability to grasp large purposes.
- 7—Ability to work intellectually, without emotional interferences of a personal or social nature.
- 8—A critical point of view toward self and work.

EDWIN E. SLOSSON

Principles and Practice of Fur Dressing and Fur Dyeing. By WILLIAM E. AUSTIN. 191 pp. D. Van Nostrand Co., New York, 1922. Price, \$4.00.

The dyeing and dressing of furs was formerly a European industry and previous to the war was of minor consideration in this country. However, owing to the serious dislocations of markets brought about by the war, the center of the fur industry has been transplanted to this country, with the result that the processing of furs here has now become an industry of large dimensions.

Fur dyeing and dressing has long been one of those "secret" arts practiced by handicraftsmen in a limited and closed guild. The literature heretofore available on this subject has been very meager.

The present volume gives us much better information than is obtainable from any preceding literature, and while the author has no doubt made good use of the sample cards issued by the various dyestuff manufacturers, he has also brought together a good deal of information that has doubtless been derived from his own experiences in the laboratory and factory. The methods of preparation used for getting the pelt into shape for dyeing are especially well considered. The actual processes of dyeing and dressing for the various types of furs are, however, rather sketchy and general in character. The book is well compiled and will be of value to the dyestuff chemist and others who desire to gain an elementary knowledge of fur dyeing. It should also be useful as a guide to students who are fitting themselves to become dyers of furs; in the latter case, however, it would be necessary to undergo considerable practical training in the handling and processing of furs.

To those dealing in and handling furs, who also desire to obtain some accurate information concerning their products, this volume will be of distinct value, as it will give them a better idea than they could otherwise obtain of the various processes and treatments necessary for the production of a finished fur.

J. MERRITT MATTHEWS

COMMERCE REPORTS

Notice—Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is \$3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.

August

The following statistics are given showing the total imports of petroleum products into Germany: 1913, 81,743 tons; 1920, 253,358 tons; and for the 12 mo. ended April 1922, 812,956 tons. The 1913 exports appear to be considerably less than the post-war figures. (P. 381)

The consumption of gasoline in Latin-American countries is reviewed and statistics are given relative to consumption, production, and importation. (Pp. 381-3)

The consumption of fertilizers in Italy is described, and statistics given. (P. 383)

Prices of phosphoric acid in Germany are given. (P. 383)

Trieste is reported as a possible distribution center for Rumanian oil. (P. 384)

A translation of the new Peruvian regulations governing petroleum concessions is on file in the Petroleum Division of the Bureau of Foreign and Domestic Commerce. (P. 384)

A French presidential decree, dated June 14, modifies the import duties on the following products: fixed oils, pure; mineral wax or ozokerite; paraffin wax; aluminium sulfate; milk sugar; and manufactures of pure copper, brass, or other copper alloys not specified in the tariff. For the most part, the changes made are by way of reduction. (P. 408)

The Minister of Trade and Customs of Australia has issued a departmental by-law providing the conditions under which amyl alcohol and fusel oil may, when denatured, be exempted from excise duty. (P. 409)

The Sicilian sulfur industry is reviewed. (Pp. 414-5)

A merger has recently been effected between four important Italian companies manufacturing and trading in tartaric acid. (P. 416)

As a result of an exploring expedition, it has been definitely ascertained that chicle and gutta percha are to be found in the forests of the Amazon River District. (P. 421)

The organization of a Chemical Division in the Bureau of Foreign and Domestic Commerce is announced, the objects of the Division are stated, and export figures for the fiscal year are given for chemicals and allied products, dyes and paints, medicines, fertilizers and naval stores. (Pp. 432-3)

The German potash industry shows a considerable improvement since the beginning of the year, a demand for German potash having arisen in both the domestic and foreign market, particularly from America. (Pp. 433-4)

Mineral production in the province of Quebec during 1921 was curtailed by circumstances which affected all branches of the trade throughout the world. The following tabular statement shows the quantity and value of the production of mineral substances in that province during 1920 and 1921: (P. 453)

ARTICLES	1920		1921	
	Quantity	Value	Quantity	Value
MINERAL SUBSTANCES				
Asbestos, tons.....	179,891	\$14,749,048	84,475	\$5,199,789
Asbestic, tons.....	19,716	43,559	12,397	14,536
Chromite, tons.....	10,585	247,730	1,893	22,696
Copper and sulfur ore, tons.....	15,186	98,854	1,986	10,463
Dolomite, tons.....	1,167	8,001
Feldspar, kaolin, and fire clay, tons.....	1,723	27,933	9,955	81,739
Gold, oz.....	935	19,346	648	12,317
Graphite, lbs.....	466,420	31,913	84,684	2,422
Magnesite, tons.....	17,941	512,755	4,984	74,110
Mica, lbs.....	1,946,399	281,729	288,197	42,222
Mineral paints, tons.....	19,185	136,098	8,894	90,765
Mineral water, gal.....	20,811	9,962	14,621	5,339
Phosphate, tons.....	30	453
Quartz and silica rock, tons.....	24,865	60,147	6,496	29,906
Silver, oz.....	57,514	58,032	39,327	21,339
Talc, tons.....	150	1,050
Titaniferous iron ore, tons.....	960	2,999
Zinc and lead ore, tons..	3,015	56,927	15,500	18,080

Improved transportation facilities are needed for the Algerian phosphate mining industry. (Pp. 453-4)

Statistics are given showing the mineral production of Italy for 1913, 1918, and 1921. (Pp. 454)

According to a cabled dispatch from the Commercial Attaché at Tokyo, no legislative action to protect the Japanese dye industry against foreign imports is likely for some time. (P. 482)

Proposed export duties on iron and copper ores included in a bill recently introduced in the Chilean Chamber of Deputies are given. (Pp. 483-4)

The provisions of the French law, by which by-products of mineral oil intended for feeding motors and for construction and maintenance of roads are admitted at a reduced rate of duty and under certain conditions, have been extended to Martinique. (P. 484)

A presidential decree extends indefinitely the concession for the importation of gasoline into Mexico free of duty. (P. 484)

Marked improvement is manifested in chemicals in France, with prices firmer and a strong demand. Many wood distillation plants, which were recently almost idle, are now working at full capacity, and the construction of new plants is planned. The glue industry is improving but exports of pharmaceutical products are meeting with severe German competition, particularly in South America. Rosin and turpentine prices are subject to considerable fluctuation, with a general upward tendency. (P. 511)

The production of copper in the Belgian Congo in 1921 exceeded 30,000 metric tons, compared with 18,500 metric tons in 1920. This is said to be due to the high percentage of copper in the ore treated. (P. 518)

The gasoline trade of the Far East is reviewed and statistics are given showing the imports, exports, and consumption. (Pp. 528-9)

The Anglo-Persian Oil Company has obtained from the Greek government exclusive rights to drill for oil over the whole of Macedonia. (P. 530)

The Red Star Refineries at Montreal have secured the Canadian rights for the manufacture of a new product (Super-Gas), which it is claimed will supplant gasoline. (P. 530)

Talk is revived that the oil shale deposits of Pictou County, Nova Scotia, may be developed at an early date through the Anglo-Persian Oil Company. These shales are reported to be rich in oil, averaging from 20 to 100 gal. per ton, with valuable by-products in addition. (P. 530)

The Special Commissioner for Railways, Eastern Africa, has published an interesting statement showing comparative costs of wood, coal, and oil as locomotive fuel on the Uganda Railway. This report indicates that fuel oil would be more economical than wood and coal. (P. 530)

A number of German firms which formerly produced explosives for military purposes are now making artificial silk from various fabrics. (P. 532)

In general, there was an increase over last year in the quantity of chemicals imported into the United Kingdom during the first six months of 1922. The most important exceptions were crude glycerol, nickel oxide, sodium compounds, and cream of tartar. Statistics are given showing in detail the imports into and the exports from the United Kingdom for the six months ended June 1921 and June 1922. (Pp. 546-7)

There is said to be a good market for American rosin in Chile. (P. 547)

Caustic soda, liquid and solid, and calcined soda are no longer subject to the import license of Switzerland. (P. 559)

A rise in French naval stores prices is noted. Stocks of turpentine on hand seem to be limited, and the heavy rains in March and April greatly retarded distillation at the opening of the season. (P. 604)

During the past two or three months, large quantities of caustic soda have been received at the port of Hamburg, about one-half of which came from the United States. German importing concerns are purchasing all consignments obtainable, the reason apparently being the endeavor of soap, glass, and chemical factories to maintain their production at capacity. (P. 604)

The Chemical Division of the Bureau of Foreign and Domestic Commerce has received a copy of Report No. 7 of the Ministry of Munitions on the "Manufacture of Nitric Acid from Niter and Sulfuric Acid." This report is based on experiments and records of the British government plants during the war and is said to be of interest to domestic manufacturers of nitric acid. A copy of this report may be borrowed from the Chemical Division for a short time. (P. 604)

Prices for sulfuric acid in Germany have been fixed by the committee for the control of sulfuric acid at 245 marks for producers and 270 marks for consumers for each 100 kilos of 60° sulfuric acid. (P. 604)

The petroleum trade of the Fiume District is reviewed. (P. 605)

The outstanding features of the petroleum import trade of the United Kingdom continue to be the increases in the imports of crude petroleum and of motor spirit. (P. 605)

The petroleum price war has now been settled in Japan by an agreement among the companies. (P. 606)

There has been a progressive increase in the production of

mineral oil in France since the first part of 1921. The production for the first three months of 1922 is said to have been 53 per cent above that for the corresponding period of 1921. (P. 606)

The tax on copra exported from Fiji has been reduced. (P. 620)

The government of British Honduras has established a King's warehouse temporarily for inflammable liquids. (Pp. 621-2)

A good market is reported in Japan for soaps, perfumes, and toilet articles. (P. 627)

SPECIAL SUPPLEMENTS ISSUED

CZECHOSLOVAKIA	HONGKONG
GUATEMALA	RUSSIAN FOREIGN TRADE
FRANCE	

"Rubber Situation in British Colonies and Protectorates." *Trade Information Bulletin* 49.

"Rumanian Petroleum Industry in 1921." *Trade Information Bulletin* 45.

STATISTICS OF EXPORTS TO THE UNITED STATES

LONDON—(P. 497)	CANADA—(P. 537)
Tin	Rubber
Drugs and chemicals	Leather
	Hides
	Wood pulp
	Pulp wood

CURRENT PUBLICATIONS

NEW BOOKS

Analytical Chemistry: Trattato di Chimica Analitica Applicata. Vol. II. G. V. VILLAVECHIA. 2nd edition, revised and enlarged. 884 pp. Price, paper, 58 lire. U. Hoepli, Milan.

Chemical Analysis: Standard Methods of Chemical Analysis. Vols. I and II. WILFRED W. SCOTT. 714 and 680 pp. Price, \$10.00. D. Van Nostrand Co., New York.

Chemistry: The Science of Matter and Its Changes. HIPPOLYTE GRUENER. 384 pp. Illustrated. Price \$3.00. Harper & Bros., New York.

Chemistry: Second Year College Chemistry. A Manual of Laboratory Exercises. WILLIAM H. CHAPIN. 122 pp. Illustrated. Price, \$1.50. John Wiley & Sons, Inc., New York.

Dust Explosions. DAVID J. PRICE and HAROLD H. BROWN. 320 pp. Illustrated. Price, \$3.00. National Fire Protection Association, Boston.

Electrochemistry: Grundzüge der Angewandten Elektrochemie. Vol. I—Elektrochemie der Lösungen. G. GRUBE. 268 pp. Price, paper, 8s. 6d.; bound, 10s. 3d. Th. Steinkopff, Dresden and Leipzig.

Evolution of Atoms and Isotopes. W. D. VERSCHOYLE. 49 pp. Price, 1s. 9d. J. J. Keliher and Co., Ltd., London.

Explosives: Technical Records of Explosives Supply. 1915 to 1918. No. 7. Manufacture of Nitric Acid from Nitric and Sulfuric Acid. 86 pp. H. M. Stationery Office, London. Price, 11s.

Filtration. T. ROLAND WOLLASTON. 102 pp. Price, 2s. 6d. Sir Isaac Pitman & Sons, Ltd., London.

Glass: Experimental Researches and Reports. Vol. IV, 1921. DEPT. OF GLASS TECHNOLOGY, The University, Sheffield. 118 pp.

Inorganic Chemistry. H. G. DENHAM. 683 pp. Price, 12s. 6d. Edward Arnold & Co., London.

Liquid Fuel and Its Apparatus. WILLIAM H. BOOTH. 2nd edition. 308 pp. Price, \$4.00. E. P. Dutton & Co., New York.

Mechanical Handling and Storing of Material. G. F. ZIMMER. 804 pp. Crosby, Lockwood & Son, London.

Paint: Proceedings of the Scientific Section, Educational Bureau. HENRY A. GARDNER, Director. 481 pp. Price, \$6.00. Quantity limited. Institute of Paint and Varnish Research, Washington, D. C.

Paint: Pour le Peintre-Vitrier: Origine, Composition et Propriétés des Matières Premières Recettes, Formulas, Procédés, "Trucs" et Tours de Main du Praticien. ED. BATAILLE, A. CHAPLET, and J. DE THELLESME. 164 pp. Illustrated. Price, 7 fr. Dunod, Paris.

Paint: Couleurs, Peintures et Vernis. J. DESALME and L. PIERRON. 455 pp. Illustrated. Price, 15 fr. Dunod, Paris.

Patent Business: A Comprehensive Instruction Course in Ten Lessons; Written for Those Who Have the Gift of Inventive Talent, and the Ambition to Supplement That Gift with a Working Knowledge of the Business of Obtaining Sound and Salable Patents as a Lifetime Occupation. Vol. I. CHARLES O. TESSIER. 155 pp. Price, \$3.00. C. O. Tessier, Cleveland, Ohio.

Potter's Craft. CHARLES F. BINNS. 206 pp. Price, \$2.50. D. Van Nostrand Co., New York.

Proceedings of the Physical Society of London. Vol. 34, Part 5. 30 pp. Price, 6s. The Fleetway Press, London.

Quicksilver, 1913-1919. The Mineral Industry of the British Empire and Foreign Countries. War Period. IMPERIAL MINERAL RESOURCES BUREAU. Price, 1s. H. M. Stationery Office, London.

Rolling Mill: Études sur les Laminoirs. J. PUPPE. 307 pp. Price, 70 fr. Dunod, Paris.

Wood Preserving Terms. ERNEST F. HARTMAN and E. F. PADDOCK. 85 pp. Price, paper, \$1.00. Protexol Corporation, New York.

RECENT JOURNAL ARTICLES

Accuracy of Boiler Tests. ALFRED COTTON. *The Coal Industry*, Vol. 5 (1922), No. 8, pp. 367-71.

Art of Alloying. W. GUERTLER. *Brass World*, Vol. 17 (1922), No. 8, pp. 229-34. Abstracted from *Zeitschrift für Metallkunde*, Vol. 9 (1921), p. 257.

Atomic Structure: The Stability of Atom Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS. *Journal of the Franklin Institute*, Vol. 194 (1922), No. 2, pp. 165-211.

Ammoniacal Liquor Stills: Observations on the Design and Working of Ammoniacal Liquor Stills. P. PARRISH. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 14, pp. 229T-42T.

Catalysts: Notes on the Poisoning of Catalysts. ALWYN PICKLES. *The Chemical Age (London)*, Vol. 7 (1922), No. 164, pp. 164-65.

Chalcedony: The Products of the Calcination of Flint and Chalcedony. EDWARD W. WASHBURN and LOUIS NAVIAS. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 9, pp. 565-85.

Chemical Change and Catalysis. Rhapsodies Culled from the Thionic Epos. HENRY E. ARMSTRONG. First Messel Memorial Lecture. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 15, pp. 253T-70T.

Chemistry and the Destruction of Pests in Agriculture. L. CARPENTER. *The Chemical Age (London)*, Vol. 7 (1922), No. 166, pp. 233-34.

Coal: The Constitution of Coal. MARIE CARMICHAEL STOPES. *The Canadian Mining Journal*, Vol. 43 (1922), No. 31, pp. 505-06.

Dye Situation in Great Britain, and Elsewhere. ELLWOOD HENDRICK. *Chemical and Metallurgical Engineering*, Vol. 27 (1922), No. 10, pp. 494-96.

Evaporation: The General Problem of Evaporation. J. W. HINCHLEY. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 14, pp. 242T-46T.

Ferrotungsten: Analise Rapida del Ferro-tungsteno. LUIGI LOSANA and ENRICO CAROZZI. *Giornale di Chimica Industriale ed Applicata*, Vol. 4 (1922), No. 7, pp. 299-301.

Fuel Oil: Distribution of Fuel Oil in Industrial Plants. J. A. BROWN. *Forging and Heat Treating*, Vol. 8 (1922), No. 8, pp. 336-40.

Glass: The British Glass Industry: Its Development and Its Outlook. W. E. S. TURNER. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 22, pp. 108-46.

- Glass:** A Critical Review of the Provisional Specifications for Glass Refractory Materials. W. J. REES. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 22, pp. 181-204.
- Glass:** The Effect of Absorbed Gas on the Conductivity of Glass. V. BUSH AND L. H. CONNELL. *Journal of the Franklin Institute*, Vol. 194 (1922), No. 2, pp. 231-40.
- Glass:** The Production of Colourless Glass in Tank Furnaces with Particular Reference to the Use of Selenium. Part I. A. COUSEN AND W. E. S. TURNER. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 22, pp. 168-81.
- Leather:** Science of Hide Curing. GEORGE D. McLAUGHLIN AND EDWIN R. THEIS. *Journal of the American Leather Chemists' Association*, Vol. 17 (1922), No. 8, pp. 376-99.
- Leaching Ore with Sulfur Dioxide.** JOSEPH IRVING, JR. *Engineering and Mining Journal-Press*, Vol. 114 (1922), No. 9, pp. 360-64.
- Lime for Glass-Making.** R. R. SHIVELY. *The Glass Industry*, Vol. 3 (1922), No. 8, pp. 154-56.
- Lubricants:** Technical Examination of Lubricating Oil and Grease. F. W. WATSON AND H. D. BELL. *The Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. 22 (1922), No. 11, pp. 211-19.
- Paper:** Rosin Size Control. P. W. CODWISE. *Paper*, Vol. 30 (1922), No. 23, pp. 7-9.
- Rubber:** Accelerated Aging Tests on Rubber Goods. W. W. EVANS. *The Rubber Age*, Vol. 11 (1922), No. 10, pp. 345-47.
- Rubber:** Scientific Management for Rubber Manufacturers. Standardization. ALFRED BARUCC. *The Rubber Age*, Vol. 11 (1922), No. 10, pp. 348-51.
- Steel:** The Annealing of Tool Steels. ARTHUR W. F. GREEN. *Forging and Heat Treating*, Vol. 8 (1922), No. 8, pp. 346-53.
- Steel:** The Making, Forging, and Heat Treating of Nickel Chromium Steels. HARRY BREARLEY. *Forging and Heat Treating*, Vol. 8 (1922), No. 8, pp. 341-45.
- Textiles:** The Acid Treatment of Cotton Fabrics for the Production of Special Finish. BARRINGTON DE PUYSTER. *Color Trade Journal*, Vol. 11 (1922), No. 2, pp. 54-59.
- Titration:** Studies in the Titration of Acids and Bases. J. L. LIZIUS. *The Analyst*, Vol. 47 (1922), No. 557, pp. 331-41.
- Wood:** The Effect of Chemicals on the Ignition Temperature of Wood. W. O. BANFIELD AND W. S. PRICK. *Canadian Chemistry and Metallurgy*, Vol. 6 (1922), No. 8, pp. 172-76.

GOVERNMENT PUBLICATIONS

Notice—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.

Bureau of Mines

- Comminuted Smokeless Powder as a Blasting Agent.** C. E. MUNROE AND S. P. HOWELL. *Reports of Investigations* 2386. 19 pp. Issued August 1922.
- Compressed-Air Illness and Its Engineering Importance with a Report of Cases at the East River Tunnels.** EDWARD LEVY. *Technical Paper* 285. 48 pp. 1922. Paper, 10 cents.
- Experimental Production of Alloy Steels.** H. W. GILLET AND E. L. MACK. *Bulletin* 199. 81 pp. Paper, 15 cents.
- Explosives Used in June 1922.** W. W. ADAMS. *Reports of Investigations* 2387. 5 pp. Issued August 1922.
- Fatalities at Coal Mines in June 1922.** W. W. ADAMS. *Reports of Investigations* 2379. 3 pp. Issued July 1922.
- Fuel Economy from Old Plant Equipment.** A. R. MUMFORD. *Reports of Investigations* 2373. 4 pp. Issued July 1922.
- Inclusions in Aluminium-Alloy Sand Castings.** R. J. ANDERSON. *Technical Paper* 290. 25 pp. 1922. Paper, 10 cents.
- Keeping Up-to-Date in Safety Methods in Coal Mining.** D. HARRINGTON. *Reports of Investigations* 2372. 2 pp. Issued July 1922.
- Permissible Explosives, Mining Equipment, and Apparatus, Approved Prior to March 15, 1922.** S. P. HOWELL, L. C. ILSLEY, D. J. PARKER, AND A. C. FIELDER. *Technical Paper* 307. 21 pp. 1922. Paper, 5 cents.
- Production of Explosives in United States, Calendar Year 1921, with Notes on Mine Accidents Due to Explosives.** W. W. ADAMS. *Technical Paper* 313. 25 pp. Paper, 5 cents.
- Recent Progress in the Thawing of Frozen Gravel in Placer Mining.** CHAS. JANIN. *Technical Paper* 309. 34 pp. 1922. Paper, 10 cents.
- Safe Mechanical Equipment for Use in Shaft Sinking.** R. H. KUDLICH. *Technical Paper* 276. 12 pp. 1922. Paper, 5 cents.
- Sixth Semiannual Motor Gasoline Survey.** A. D. BAUER AND N. F. LE JBUNN. *Reports of Investigations* 2388. 9 pp. Issued August 1922.

- Storage and Transportation of Portland Cement.** (With a Bibliography.) W. M. MYERS. *Reports of Investigations* 2377. 5 pp. Issued July 1922.
- Summary of Investigations of Dust and Ventilation in Metal Mines.** (With a Bibliography.) *Reports of Investigations* 2374. 6 pp. Issued July 1922.
- The Rate of Reduction of Hematite to Magnetite by Methane.** C. M. BOUTON. *Reports of Investigations* 2381. 9 pp. Issued August 1922.
- Why Miners' Portable Electric Lamps Require Safety Devices.** L. C. ILSLEY. *Reports of Investigations* 2371. 9 pp. Issued July 1922.

Bureau of Standards

- Practical Spectrographic Analysis.** W. F. MEGGERS, C. C. KIESS, AND F. J. STIMSON. *Scientific Paper* 444. 1922. Paper, 10 cents.
- Radiators for Aircraft Engines.** S. R. PARSONS AND D. R. HARPER, 3RD. *Technologic Paper* 211. 183 pp. Paper, 50 cents.
- The Spectral Transmissive Properties of Dyes: I—Seven Permitted Food Dyes, in the Visible, Ultraviolet, and Near Infra-Red.** K. S. GIBSON, H. J. McNICHOLAS, E. P. T. TYNDALL, M. K. FRÉHAFER, with the co-operation of W. E. MATHEWSON. *Scientific Paper* 440. 184 pp. Paper, 15 cents.
- United States Government Specification for Automobile Soap.** *Circular* 127. Paper, 5 cents.
- United States Government Specification for Basic Carbonate White Lead, Dry and Paste, Federal Specifications Board, Standard Specification 5.** Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government, in purchase of materials covered by it. *Circular* 84. 2nd ed. 8 pp. Paper, 5 cents.
- United States Government Specification for Chip Soap.** *Circular* 128. 1922. Paper, 5 cents.
- United States Government Specification for Flat Interior Lithopone Paint, White and Light Tints, Federal Specifications Board, Standard Specification 21.** Officially Adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 111. 3rd ed. 8 pp. Paper, 5 cents.
- United States Government Specification for Grit Cake Soap.** *Circular* 130. 1922. Paper, 5 cents.
- United States Government Specification for Hand Grit Soap.** *Circular* 130. 1922. Paper, 5 cents.
- United States Government Specification for Interior Varnish, Federal Specifications Board, Standard Specification 22.** Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 117. 6 pp. Paper, 5 cents.
- United States Government Specification for Iron-Oxide and Iron-Hydroxide Paints, Federal Specifications Board, Standard Specification 13.** Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 93. 2nd ed. 9 pp. 1922. Paper, 5 cents.
- United States Government Specification for Leaded Zinc Oxide, Dry and Paste, Federal Specifications Board, Standard Specification 9.** Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 88. 2nd ed. 8 pp. 1922. Paper, 5 cents.
- United States Government Specification for Linseed Oil, Raw, Refined, and Boiled, Federal Specifications Board, Standard Specification 4.** Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of Government in purchase of materials covered by it. *Circular* 82. 2nd ed. 9 pp. Paper, 5 cents.
- United States Government Specification for Liquid Soap.** *Circular* 124. 1922. Paper, 5 cents.
- United States Government Specification for Ocher, Dry and Paste, Federal Specifications Board, Standard Specification 12.** Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 91. 2nd ed. 8 pp. Paper, 5 cents.
- United States Government Specification for Ordinary Laundry Soap.** *Circular* 129. 1922. Paper, 5 cents.
- United States Government Specification for Salt Water Soap.** *Circular* 126. 1922. Paper, 5 cents.
- United States Government Specification for Scouring Compounds, for Floors (a) and (b), and Soap Scouring Compound (c).** *Circular* 131. 1922. Paper, 5 cents.
- United States Government Specification for Soap Powder.** *Circular* 125. Paper, 5 cents.
- United States Government Specification for White Floating Soap.** *Circular* 123. Paper, 5 cents.

Bureau of the Census

- Glucose and Starch. 14th Census of the United States: Manufacturers, 1919. Prepared under the supervision of E. F. HARTLEY. 8 pp. 1922.
- Gold, Silver, Copper, Lead, and Zinc. 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. HARTLEY by F. J. KATZ. 33 pp. 1922.
- Iron Ore. 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. HARTLEY by F. J. KATZ. 25 pp. 1922.
- Petroleum and Natural Gas. 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. HARTLEY by F. J. KATZ. 31 pp. 1922.
- Petroleum Refining. 14th Census of the United States: Manufacturers, 1919. Prepared under the supervision of E. F. HARTLEY. 11 pp. 1922.

Congress

- An Act, to regulate revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes. *H. Rpt.* 7456. August 19, 1922. Ordered to be printed with the amendments of the Senate numbered. 476 pp.
- A Bill, to improve the navigability of waters of the United States by preventing oil pollution thereof. S. 3968. Introduced by Mr. Frelinghuysen on August 30, 1922. Read twice and referred to the Committee on Commerce. 4 pp.
- Muscle Shoals. Mr. Ladd (for himself and Messrs. Capper, Harrison, Caraway, Ransdell, Heflin, and Smith), from the Committee on Agriculture and Forestry, submitted views to accompany S. J. Res. 227. Calendar 817. *S. Rpt.* 831. Part 2. 19 pp. August 4, 1922.
- Muscle Shoals. Hearings on S. 3420, for manufacture of explosives, for use of Army and Navy, for manufacture of fertilizer, for agricultural purposes, to incorporate Federal Chemical Corporation, and for other purposes; and on the Henry Ford Muscle Shoals offer, offer made by the Alabama Power Co., proposing to complete Wilson Dam, the offer of Frederick E. Engstrom for Muscle Shoals, and offer of Charles L. Parsons for properties at Muscle Shoals, Ala. 949 pp. 1922.
- Muscle Shoals. Report to accompany S. J. Res. 227 (rejecting bids for acquisition of Muscle Shoals); submitted by Mr. Norris, April 20, 1922, calendar day July 20, 1922. *S. Rpt.* 831. Part 1. 36 pp.
- Salt peter, Chile. Nitrate of soda imports from Chile to United States, extracts from hearings, 66th Congress, 2nd Session, and 67th Congress, 2nd session. 1 p.
- Water Pollution. Preventing the Oil Pollution of Navigable Waters of the United States. *S. Rpt.* 901, to accompany S. 3968. August 31, 1922. 3 pp.

Department of Agriculture

- By-products from Crushing Peanuts. J. B. REED. *Department Bulletin* 1096. 12 pp. Issued August 12, 1922.
- Digestibility of Cod-Liver, Java-Almond, Teaseed, and Watermelon-Seed Oils, Deer Fat, and Some Blended Hydrogenated Fats. H. J. DRUEL, JR. *Department Bulletin* 1033. 15 pp. Paper, 15 cents. Issued July 27, 1922.
- Rules and Regulations for the Enforcement of the Federal Food and Drugs Act. *Circular* 21. Office of the Secretary. 8th revision. 27 pp. Issued August 7, 1922.
- Some Experiments with a Boric Acid-Canning Powder. R. B. EDMONDSON, CHARLES THOM, AND L. P. GILTNER. *Department Circular* 237. 12 pp. Issued August 31, 1922. Paper, 5 cents.

Federal Trade Commission

- Petroleum Trade in Wyoming and Montana. Letter transmitting, pursuant to law, report on conditions in petroleum trade in Wyoming and Montana (with draft of bill to prevent evasions of antitrust laws). *S. Doc.* 233. 4 pp. 1922.

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- Bauxite and Aluminium in 1921. J. M. HILL. Separate from Mineral Resources of the United States, 1921, Part 1. 8 pp. Published August 1, 1922.
- Clay-Working Industries. Clay, and Silica Brick in 1919 and 1920. JEFFERSON MIDDLETON. Separate from Mineral Resources of the United States, 1920, Part 2. 37 pp. Published August 14, 1922.
- Gypsum in 1921. K. W. COTTRELL. Separate from Mineral Resources of the United States, 1921, Part 2. 8 pp. Published August 4, 1922.
- Magnesite in 1921. C. G. YALE. Separate from Mineral Resources of the United States, 1921, Part 2. 6 pp. Published August 5, 1922.

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- Oil and Gas Prospects in and near the Crow Indian Reservation, Montana. W. T. THOM, JR. *Bulletin* 736-B. Separate from Contributions to Economic Geology, 1922, Part 2. 19 pp. Published July 6, 1922.
- Quicksilver in 1921. F. L. RANSOME. With a Bibliography by I. P. EVANS. Separate from Mineral Resources of the United States, 1921, Part 1. 14 pp. Published August 7, 1922.
- Tin in 1921. B. L. JOHNSON. Separate from Mineral Resources of the United States, 1921, Part 1. 3 pp. Published August 1, 1922.

Interior Department

- Naval Reserve Oil Leases, in Response to Resolution. Communication submitting information concerning Naval Reserve Oil Leases. *S. Doc.* 210. 42 pp. 1922.

Public Health Reports

- Ohio Law for Enforcing Correction of Stream Pollution and Improvement of Public Water Supplies. *Public Health Reports*, 37 (August 11, 1922), 1945-50.
- Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide. R. R. SAYERS, F. V. MERIWETHER, AND W. P. YANT. *Reprint* 748. 16 pp. Paper, 5 cents.
- Preparation and Administration of Arsphenamine and Neoarsphenamine. Standard Instructions for the Preparation and Intravenous Administration of Arsphenamine and Neoarsphenamine for Use by the Medical Departments of the Army, of the Navy, and of the Veterans' Bureau, and by the Public Health Service. *Public Health Reports*, 37 (August 4, 1922), 1867-82.
- Report on the Public Water Supply of Delaware, Ohio. Report of an Investigation Made by the Engineering Division of the Ohio State Department of Health. F. H. WARING. *Public Health Reports*, 37 (August 11, 1922), 1933-45.
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Tariff Commission

- Tariff Information Surveys. Revised edition, 1922. On articles in Paragraph 359 of the Tariff Act of 1913 and related articles in other paragraphs.
- N-15. Heavy Leathers. 48 pp. Paper, 5 cents.
- N-16. Light Leathers, Group 1. 54 pp. Paper, 5 cents.

The Foreign Commerce Department of the Chamber of Commerce of the United States has just issued a foreign commerce handbook, which contains a great deal of valuable information as to sources of service in foreign trade. The book also contains a list of the topics of national importance that are engaging the attention of the Chamber's Foreign Commerce Department Committee.

Zinsser & Co., Hastings-on-Hudson, N. Y., are now manufacturing Aczol, a wood preservative which has been in use in Belgium and continental Europe for several years. The name is derived from its ingredients—ammonia, copper, zinc, and phenol. Records of the use of wood impregnated with Aczol have been kept in Belgium for the past decade, and it is claimed to be very efficient, particularly in coal mine timbers, wood paving blocks, and railroad ties.

A company is being organized to manufacture potassium phosphate under the Kreiss patents at Jacksonville, Fla. Work on a \$75,000 plant will begin shortly. The company will not manufacture complete fertilizers, but will sell the potassium phosphate to fertilizer manufacturers. The officers are: president, E. R. Taber; vice president, William B. Taber; secretary and treasurer, Charles N. Welshans.

E. I. du Pont de Nemours & Co. have announced the development of a dye known as Pontamine Brown CR, a direct dyestuff which produces reddish brown shades on cotton and may also be used on artificial silk.

Chemical fumes coming in contact with the flame of a night watchman's oil lamp are believed to have caused a fire which wrecked one of the buildings of the Verona Chemical Company plant at Newark, N. J., on September 1. The damage is estimated at \$100,000.

MARKET REPORT—SEPTEMBER, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

September has seen a steady strengthening in the tone of chemical markets, with a more decided upward trend to prices. Practically all the important movements during the month have been toward higher levels. Both heavy chemicals and medicinals have shared in the improved position, while intermediates and dyestuffs have continued to remain dormant. The tariff situation has naturally held the center of the stage, and, although there was some movement of goods based on rates which were considered certain prior to passage, the general attitude of consumers was to wait for definite certainties. In the chemical markets generally over a period of a month past, 80 per cent or more of all price movements have been to higher levels.

Many prices were advanced in anticipation of the tariff,—that is, the higher cost of raw materials which in a number of cases was caused by speculative buying before the higher rates went into effect, drove up figures for finished goods. A number of prices were advanced, owing to scarcities of spot goods developing through the long inactivity in manufacturing circles, permitting stocks to become almost depleted. Most consumers preferred to pay the higher prices for spot goods rather than gamble on contract supplies, with the tariff uncertainty hovering over them. Increased activity in chemical-consuming manufacturing circles broadened the hand-to-mouth buying for immediate needs and played its part in the reduction of available stocks.

Among the heavy chemicals, the mineral acids have remained unchanged and quiet. Caustic soda held strong throughout the month, but softened slightly at the close, owing to cheaper offerings in outside hands. Soda ash has been steady with a consistently good demand. Copper sulfate supplies are still closely held and not overabundant. Bleaching powder has been extremely scarce, especially on the spot, and has moved upward in price on this account from \$1.75 to \$2.00 per hundred. Arsenic prices have held tight with an advancing tendency, although the consuming season is about over. Through the season, supplies have been inadequate to supply the growing demand for this product. This year the particularly heavy demand for calcium arsenate in the cotton fields took all available arsenic supplies.

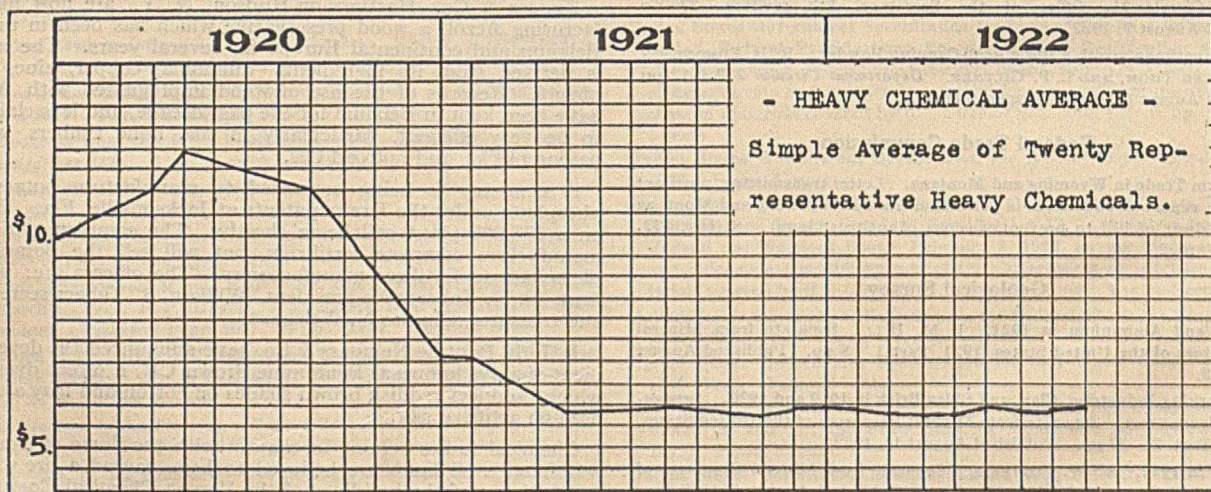
Both sodium and potassium prussiates have reached higher prices during the month. Yellow potassium prussiate moved up to 36 cents a pound spot. Bichromates are slightly higher than they were during August. Salt cake has continued scarce. Supplies of copperas, some months ago a drug on the market here, have been

cleaned up and are now very small. Producers of oxalic acid have moved their prices up to 17 cents a pound, f. o. b. works, during the month. Of the alums, ammonia is higher while the others have remained unchanged. Both ammonium sulfate and gray sal ammoniac have gained in price, as spot supplies have been taken up without replacement. In fact, all ammonium products have been strong as a result of lack of activity in the by-product plants. Little has happened in caustic potash and the market has remained quiet. Taken all in all, industrial chemical prices have gained 1 or 2 per cent during September.

Of the oils, linseed has held strong in spite of the fact that most of the big buyers have been holding off for lower prices. The price stands slightly higher than it did at the beginning of the month. Menhaden strengthened slightly on some buying. Cottonseed oil continues quiet. Turpentine moved up during the month from \$1.23 a gallon to \$1.32 after numerous fluctuations. A few minor fluctuations in rosin during the month found the price little changed at the close.

Phenol, because of its scarcity and high price for some two months past, is worthy of special attention at this time. Spot supplies of crystals are practically impossible to find on the open market. A few odd lots are available, but the only quantity stocks are reported held by two leading consumers who are evidently not anxious to sell. Licenses for import from Europe have been issued, but owing to the uncertainty of getting supplies, the new tariff rate, and the higher prices ruling abroad, consumers here are hesitating to bring in stocks. A well-known manufacturer is reported to have resumed manufacturing synthetic phenol, but if the report is true, none has yet been offered on the market from this source. Prices for odd lots of spot crystals in large drums stand to-day at 20 cents at 22 cents a pound.

In the fine chemicals, advances have been scored by the salicylates, as might be expected with the present market for phenol. The sharp rise in quicksilver prices on the almost certain prospects of an \$18.75 a flask duty, forced manufacturers of mercurials to move up their prices. Glycerin has climbed steadily. Resorcinol is higher. Wood alcohol is up sharply. Surplus stocks of formaldehyde have been cleaned out and prices are higher with goods hard to find. After a long period of weakness, hydroquinone moved up sharply. Iodine and the iodides were advanced during the month; the syndicate figure for crude iodine has been revised upward. Acetone has gone up. Imported citric and tartaric acids and cream of tartar rose on higher import cost. Bismuth salts were advanced twice in the month.



FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

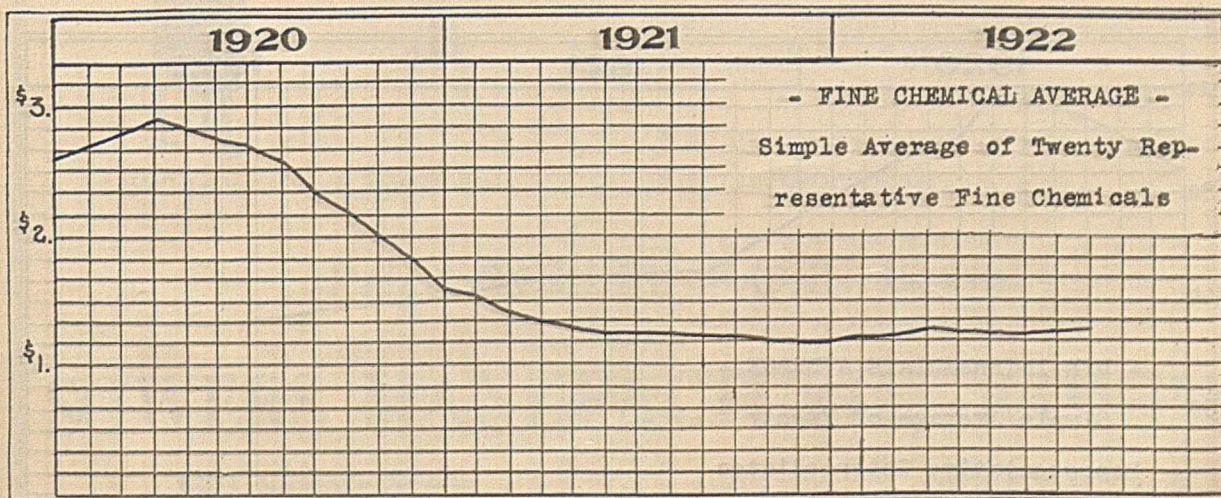
	Sept. 1	Sept. 15	Jan. 1922
Acid, Boric, cryst. bbls.lb.	.11 $\frac{3}{4}$.11 $\frac{3}{4}$.12 $\frac{3}{4}$
Hydrochloric, comm'l. 20° lb.	.01 $\frac{3}{4}$.01 $\frac{3}{4}$.01 $\frac{3}{4}$
Hydrofluoric, 30% bbls.lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/1 wks.lb.	.06	.06	.06
Phosphoric, 50% tech.lb.	.07 $\frac{1}{2}$.08	.10
Sulfuric, C. P.lb.	.08	.07	.07
66° tks. wks.ton	16.00	16.00	16.00
Oleum 20%ton	19.00	19.00	19.00
Alum, Ammonia, lump.lb.	.03 $\frac{1}{4}$.03 $\frac{1}{2}$.03 $\frac{1}{2}$
Potash, lump.lb.	*.03	*.03	*.03 $\frac{1}{2}$
Chrome.lb.	.06	.06 $\frac{1}{2}$.07
Soda, ground.lb.	.03 $\frac{1}{2}$.03 $\frac{1}{2}$.03 $\frac{1}{2}$
Aluminium Sulfate (iron-free)lb.	.02 $\frac{1}{2}$.02 $\frac{1}{2}$.02 $\frac{1}{2}$
Ammonium Carbonate, pwd.lb.	.08 $\frac{1}{2}$.07	.08
Chloride, white gran.lb.	.07 $\frac{3}{4}$.07 $\frac{3}{4}$.07 $\frac{1}{2}$
Ammonia, anhydrous.lb.	.30	.30	.30
Ammonia Water, drums, 26°lb.	.07 $\frac{1}{2}$.07 $\frac{1}{2}$.07 $\frac{1}{2}$
Arsenic, white.lb.	.08 $\frac{1}{2}$.08 $\frac{1}{2}$.06 $\frac{1}{2}$
Barium Chloride.ton	*85.00	*85.00	*53.00
Nitrate.lb.	*.08	*.08	*.07
Barytes, white.ton	33.50	33.50	28.00
Bleaching Powd., 35%, works100 lbs.	1.75	2.00	2.25
Borax, cryst., bbls.lb.	.05 $\frac{1}{2}$.05 $\frac{1}{2}$.05 $\frac{1}{4}$
Bromine, pure, wks.lb.	.28	.28	.23
Calcium Chloride, fused, f.o.b. N. Y.ton	24.50	24.50	28.75
Chlorine, liquid.lb.	.06	.06	.06
Copper Sulfate.100 lbs.	7.00	7.00	5.55
Iodine, resublimed.lb.	4.20	4.40	3.80
Lead Acetate, white crystals.lb.	.10 $\frac{1}{2}$.10 $\frac{1}{2}$.11
Nitrate.lb.	.22	.22	.15
Red.lb.	.08	.08	.08
White (Carb.)lb.	.07 $\frac{1}{4}$.07 $\frac{1}{4}$.07 $\frac{1}{4}$
Lime Acetate.100 lbs.	2.35	2.35	1.75
Magnesium Carbonate, tech.lb.	.06	.06	.06
Magnesite, calcined.ton	55.00	55.00	55.00
Phosphorus, yellow.lb.	*.25	*.25	*.27
Red.lb.	*.26	*.26	*.30
Plaster of Paris.bbl.	4.25	4.25	4.25
Potassium Bichromate.lb.	.09 $\frac{3}{4}$.09 $\frac{3}{4}$.10 $\frac{1}{2}$
Bromide, imported.lb.	*.13	*.14	*.13
Carbonate, calc., 80-85%lb.	*.04 $\frac{3}{4}$	*.04 $\frac{3}{4}$	*.04 $\frac{1}{2}$
Chlorate, cryst.lb.	*.06 $\frac{1}{2}$	*.07	*.05 $\frac{1}{2}$
Hydroxide, 88-92%lb.	*.05 $\frac{3}{4}$	*.05 $\frac{3}{4}$	*.06
Iodide, bulk.lb.	3.30	3.50	2.90
Nitrate.lb.	.08	.08	.08
Permanganate, U. S. P.lb.	*.14 $\frac{1}{2}$	*.15	*.15
Prussiate, red.lb.	*.90	*.90	*.29
Yellow.lb.	*.33	*.35	*.24 $\frac{1}{2}$
Salt Cake, bulk.ton	18.00	18.00	17.00
Silver Nitrate.oz.	.47 $\frac{1}{2}$.46 $\frac{1}{2}$.44 $\frac{1}{2}$
Soda Ash, 58%, bags.100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y.100 lbs.	3.60	3.60	3.80

*Resale or Imported (not an American makers' price).

	Sept. 1	Sept. 15,	Jan. 1922
Sodium Acetate.lb.	.06	.06	.04
Bicarbonate.100 lbs.	2.00	2.00	2.00
Bichromate.lb.	.07	.07 $\frac{1}{2}$.07 $\frac{3}{4}$
Bisulfite, powd.lb.	.04 $\frac{1}{4}$.04 $\frac{1}{4}$.04 $\frac{1}{4}$
Chlorate.lb.	.06 $\frac{1}{4}$.07	.07 $\frac{1}{2}$
Cyanide, 96-98%lb.	.23	.23	.28
Fluoride, tech.lb.	.09 $\frac{1}{2}$.09 $\frac{1}{2}$.09 $\frac{1}{2}$
Hyposulfite, bbls.100 lbs.	2.00	2.00	3.50
Nitrate, 95%100 lbs.	2.55	2.55	2.32 $\frac{1}{2}$
Nitrite.lb.	.09 $\frac{1}{2}$.09 $\frac{1}{2}$.06 $\frac{1}{2}$
Prussiate, yellow.lb.	.22	.23 $\frac{1}{2}$.16 $\frac{1}{2}$
Phosphate (di-sod.), tech.lb.	.04	.04 $\frac{1}{2}$.04 $\frac{1}{4}$
Silicate, 40°lb.	.01 $\frac{1}{2}$.01 $\frac{1}{2}$.01 $\frac{1}{4}$
Sulfide, 60%, fused.lb.	.04	.04	.05
Strontium Nitrate.lb.	*.10	*.10	*.10
Sulfur, flowers.100 lbs.	3.00	3.00	2.75
Crude, mines.long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n.lb.	.10 $\frac{1}{2}$.10 $\frac{1}{2}$.09 $\frac{3}{4}$
Oxide.lb.	.38	.38	.37
Zinc Chloride, U. S. P.lb.	.35	.35	.35
Oxide, bbls.lb.	.07	.07	.08

ORGANIC CHEMICALS

Acetanilide, U. S. P. bbls.lb.	*.29	*.29	*.29
Acid, Acetic, 28 p. c.100 lbs.	2.67 $\frac{1}{2}$	2.67 $\frac{1}{2}$	2.37 $\frac{1}{2}$
Glacial.lb.	.11	.11	.10
Benzoic, U. S. P.lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs.lb.	.20	.22	.12
50- to 110-lb. tins.lb.	.24	.24	.18
Citric, crystals, kegs.lb.	*.44 $\frac{1}{2}$	*.45	*.43
Oxalic, cryst., bbls., wks.lb.	.17	.17	.14
Pyrogallic, resublimed.lb.	1.60	1.60	1.75
Salicylic, U. S. P.lb.	.29	.29	.24
Tannic, U. S. P., bbls.lb.	.70	.70	.75
Tartaric, cryst., U. S. P.lb.	*.28 $\frac{1}{2}$	*.30	*.25
Acetone, drums.lb.	.13 $\frac{1}{2}$.16	.12
Alcohol, denatured, complete. gal.	.31	.31	.45
Ethyl, 190 proof, bbls.gal.	4.65	4.65	4.75
Amyl Acetate.gal.	2.00	2.00	2.00
Camphor, Jap, refined, cases.lb.	.83	.83	.90
Carbon Bisulfide, c/l.lb.	.06	.06	.06 $\frac{1}{2}$
Tetrachloride.lb.	.10	.10	.10 $\frac{1}{2}$
Chloroform, U. S. P., drums.lb.	.25	.25	.43
Creosote, U. S. P.lb.	.40	.40	.40
Cresol, U. S. P.lb.	.14	.14	.14
Dextrin, corn.100 lbs.	3.09	3.09	2.70
Imported Potato.lb.	.09	.09	.06 $\frac{1}{2}$
Ether, U. S. P., 100 lbs.lb.	.14	.14	.14
Formaldehyde, bbls.lb.	.08	.10	.10 $\frac{1}{2}$
Glycerol, dynamite, drums.lb.	.15	.15	.14 $\frac{1}{2}$
Methanol, pure, bbls.gal.	.72	.80	.75
Methylene Blue, med.lb.	3.00	3.00	4.00
Petrolatum, light amber.lb.	.04 $\frac{1}{2}$.04 $\frac{1}{2}$.05 $\frac{1}{4}$
Pyridine.gal.	1.75	1.75	1.75
Starch, corn, pow'd.100 lbs.	2.47	2.47	2.13
Potato, Jap.lb.	.07	.07	.08 $\frac{1}{2}$
Sago.lb.	.03 $\frac{1}{2}$.03 $\frac{1}{2}$.04



OILS, WAXES, ETC.

	Sept. 1	Sept. 15	Jan. 1922
Beeswax, pure, white.....lb.	.40	.40	.33
Castor Oil, No. 3.....lb.	.12	.12	.10½
Ceresin, yellow.....lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills...lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill.....lb.	.08½	.08½	.07
Linseed Oil, raw, c/1.....gal.	.88	.90	.89
Menhaden Oil, crude, mills...gal.	.40	.41	.35
Neat's-foot Oil, 20°.....lb.	.20	.20	.16¾
Paraffin, 128-130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "R" grade, 280 lbs... bbl.	6.30	6.30	5.30
Rosin Oil, first run.....gal.	.39	.40	.36
Shellac, T. N.....lb.	.70	.67	.66
Sperm Oil, bleached winter, 38°.....gal.	1.35	1.35	1.70
Stearic Acid, double pressed...lb.	.09½	.09½	.09¾
Tallow Oil, acidless.....lb.	.10	.10	.10
Turpentine, spirits of.....gal.	1.23	1.30	.82½

METALS

	Sept. 1	Sept. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	.17½	.17
Antimony, ordinary.....100 lbs.	5.25	6.50	4.55
Bismuth.....lb.	2.10	2.20	1.80
Copper, electrolytic.....lb.	.14	.14	.13¾
Lake.....lb.	.14	.14	.13¾
Lead, N. Y.....100 lbs.	5.75	6.05	4.70
Nickel, electrolytic.....lb.	.39	.36	.45
Platinum, refined, soft.....oz.	93.00	118.00	78.00
Quicksilver, flask.....75 lbs. ea.	62.00	66.00	52.00
Silver, foreign.....oz.	.71¾	.69	.65¾
Tin.....lb.	.32	.32	.32¾
Tungsten Wolframite... per unit	3.00	3.25	2.00
Zinc, N. Y.....100 lbs.	6.25	6.60	5.20

FERTILIZER MATERIALS

	Sept. 1	Sept. 15	Jan. 1922
Ammonium Sulfate, expt., 100 lbs.	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y... unit	4.00	4.00	3.50
Bone, 3 and 50, ground, raw... ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia.....	2.75	2.75	2.25
Fish Scrap, dried, wks.....unit	4.10 & .10	4.10 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78-80%.....ton	4.00	4.00	8.00
Potassium Muriate, 80%.....unit	.60	.60	*.75
Tankage, high-grade, f. o. b. Chicago.....unit	4.00 & .10	4.00 & .10	3.00 & .10

COAL-TAR CHEMICALS

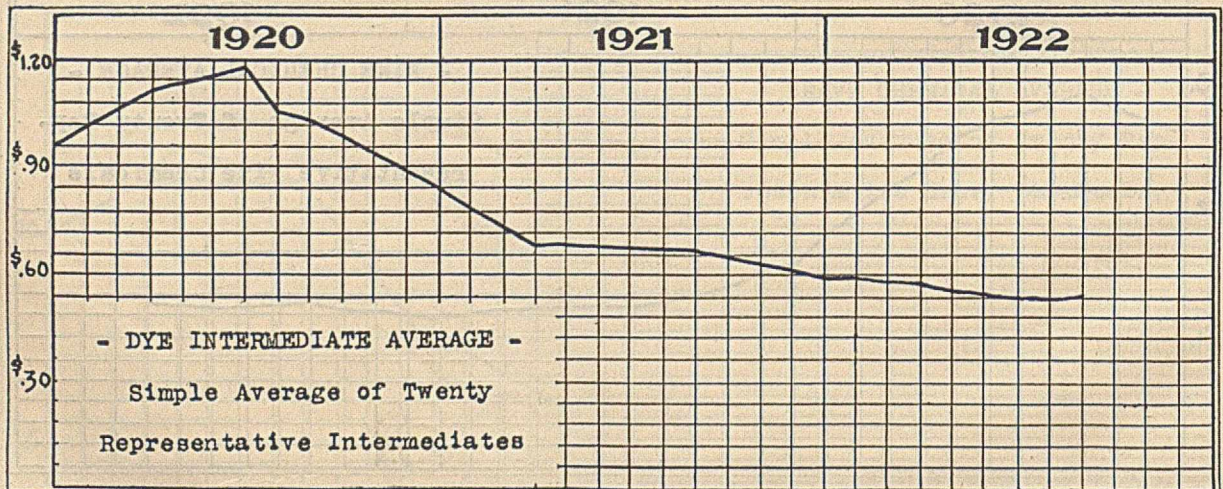
Crudes			
	Sept. 1	Sept. 15	Jan. 1922
Anthracene, 80-85%.....lb.	.75	.75	.75
Benzene, pure, tanks.....gal.	.30	.30	.29
Naphthalene, flake.....lb.	.06½	.06½	.07½
Phenol, drums.....lb.	.18	.20	.11

Crudes (concluded)

	Sept. 1	Sept. 15	Jan. 1922
Toluene, pure, tanks.....gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks.....gal.	.45	.45	.45

Intermediates

Acids:			
	Sept. 1	Sept. 15	Jan. 1922
Anthranilic.....lb.	1.10	1.10	1.10
Benzoic, tech.....lb.	.50	.50	.50
Cleve's.....lb.	1.50	1.50	1.50
Gamma.....lb.	1.80	1.80	2.25
H.....lb.	.75	.75	1.00
Metanilic.....lb.	1.00	1.00	1.60
Monosulfonic F.....lb.	2.30	2.30	2.30
Naphthionic, crude.....lb.	.60	.60	.65
Neville & Winther's.....lb.	1.20	1.20	1.30
Picric.....lb.	.20	.20	.25
Sulfanilic.....lb.	.22	.22	.26
Tobias'.....lb.	1.50	1.50	2.00
Aminoazobenzene.....lb.	1.15	1.15	1.15
Aniline Oil.....lb.	.14	.14	.17
Aniline Salt.....lb.	.20	.20	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech.....lb.	.65	.65	.45
U. S. P.....lb.	1.40	1.40	1.25
Benzidine Base.....lb.	.85	.85	.90
Benzidine Sulfate.....lb.	.70	.70	.70
Diaminophenol.....lb.	5.50	5.50	5.50
Dianisidine.....lb.	4.50	4.50	4.75
p-Dichlorobenzene.....lb.	.17	.17	.15
Diethylaniline.....lb.	.60	.60	.90
Dimethylaniline.....lb.	.32	.32	.40
Dinitrobenzene.....lb.	.20	.20	.21
Dinitrotoluene.....lb.	.20	.20	.25
Diphenylamine.....lb.	.58	.58	.58
G Salt.....lb.	.65	.65	.70
Hydroquinol.....lb.	.80	1.15	1.35
Monochlorobenzene.....lb.	.10	.10	.10
Monoethylaniline.....lb.	1.00	1.00	1.00
b-Naphthol, dist.....lb.	.22	.22	.30
a-Naphthylamine.....lb.	.30	.30	.30
b-Naphthylamine.....lb.	.95	.95	1.05
m-Nitroaniline.....lb.	.72	.72	.85
p-Nitroaniline.....lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol.....lb.	.75	.75	.75
o-Nitrotoluene.....lb.	.12	.12	.15
p-Nitrotoluene.....lb.	.60	.60	.70
m-Phenylenediamine.....lb.	1.00	1.00	1.10
p-Phenylenediamine.....lb.	1.50	1.50	1.60
Phthalic Anhydride.....lb.	.35	.35	.38
R Salt.....lb.	.55	.50	.60
Resorcinol, tech.....lb.	1.30	1.30	1.50
U. S. P.....lb.	1.75	2.00	2.00
Schaeffer's Salt.....lb.	.60	.60	.70
Sodium Naphthionate.....lb.	.60	.60	.70
Thiocarbanilide.....lb.	.35	.35	.40
Tolidine (base).....lb.	1.15	1.15	1.20
Toluidine, mixed.....lb.	.30	.30	.30
o-Toluidine.....lb.	.16	.16	.20
p-Toluidine.....lb.	1.00	1.00	1.10
m-Toluylenediamine.....lb.	.95	.95	1.10
Xylidine.....lb.	.42	.42	.40



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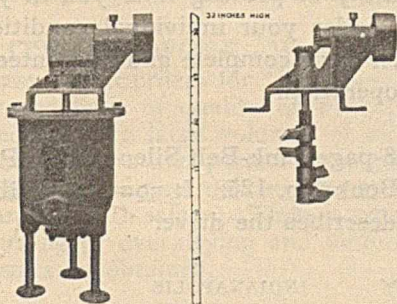
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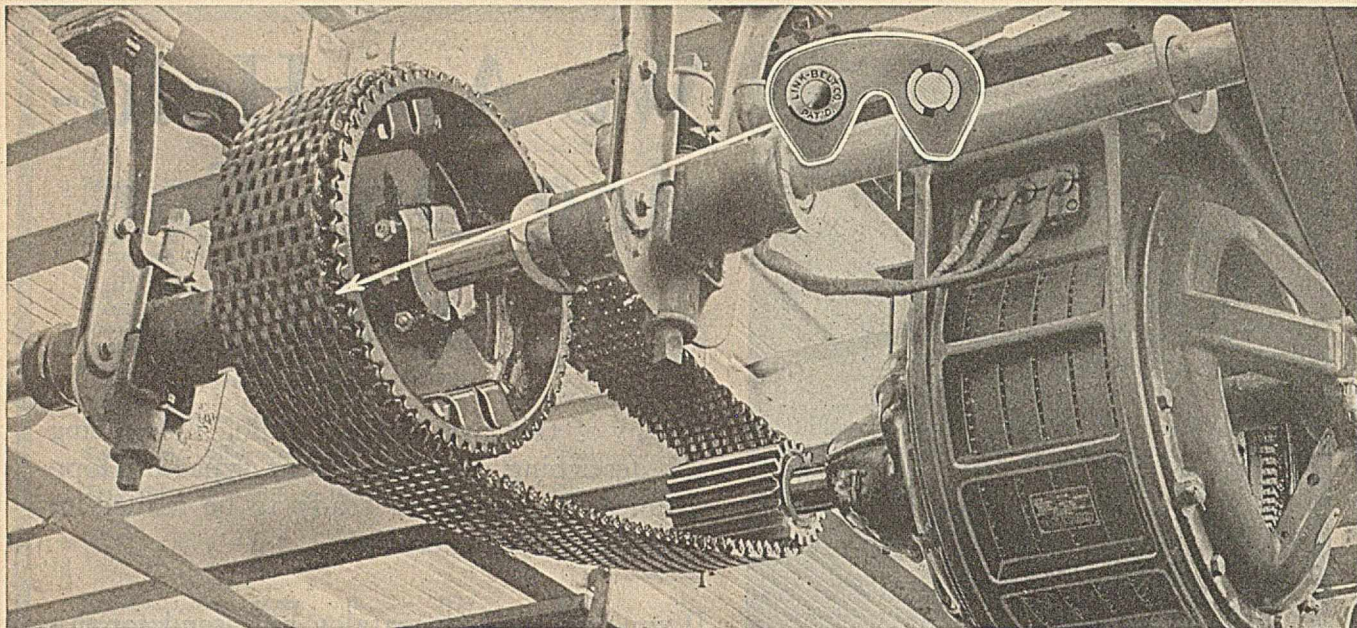
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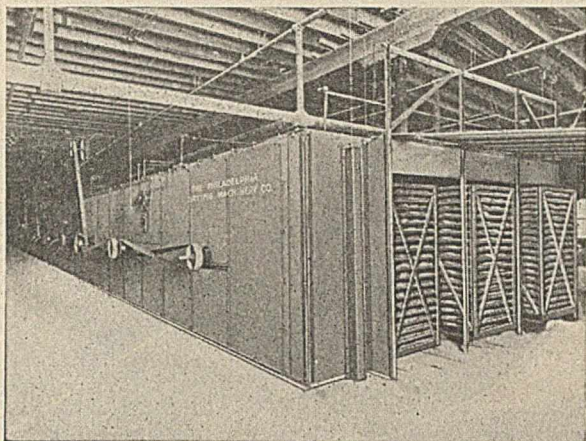
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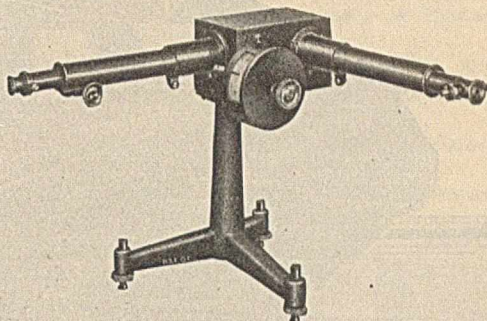
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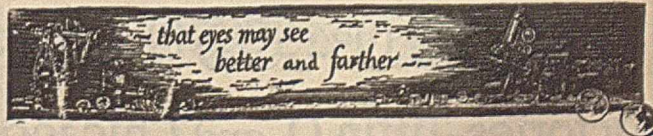
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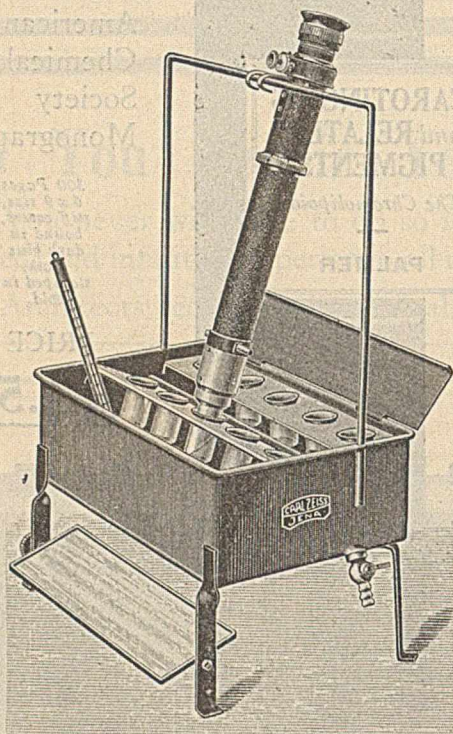
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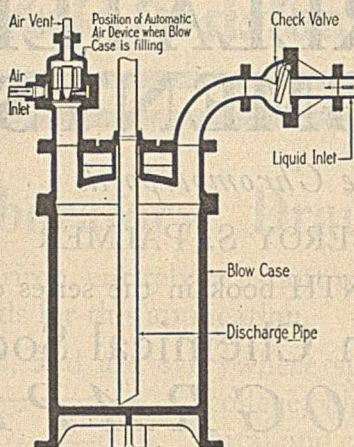


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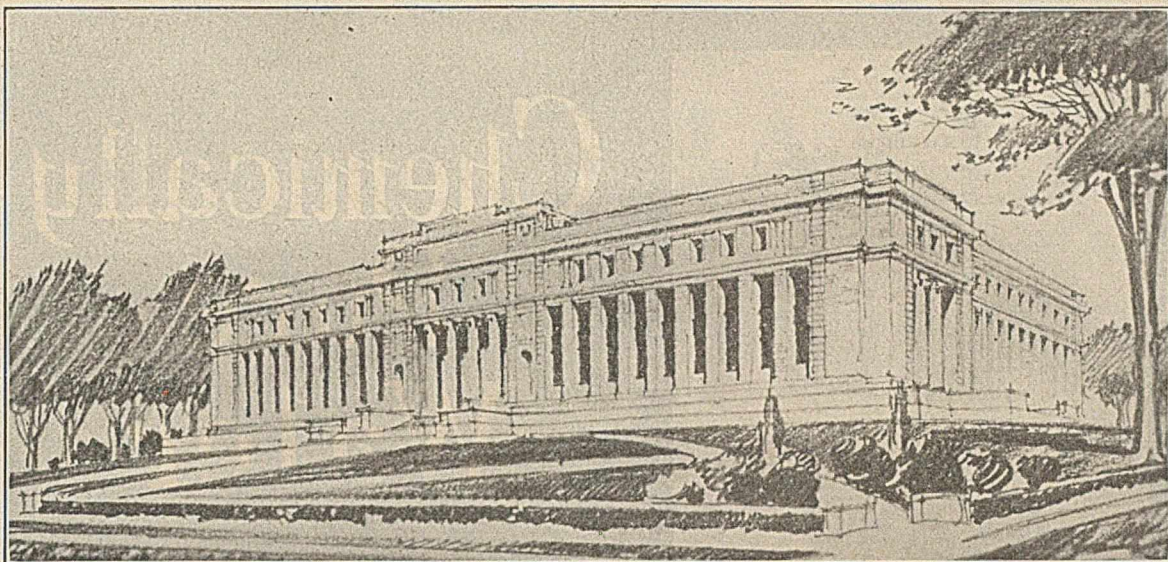
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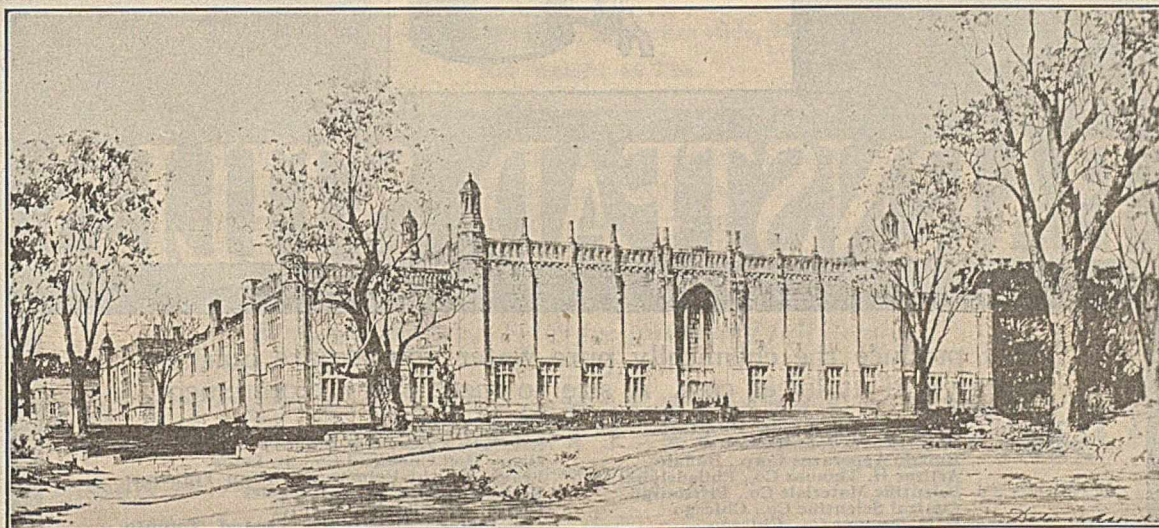
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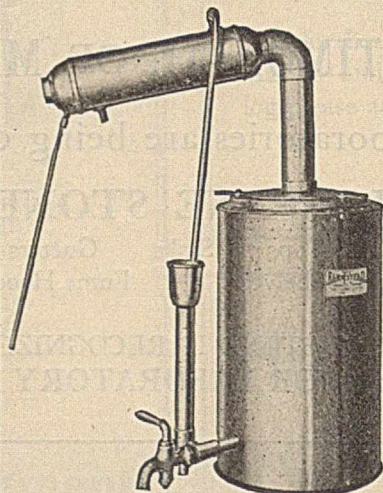
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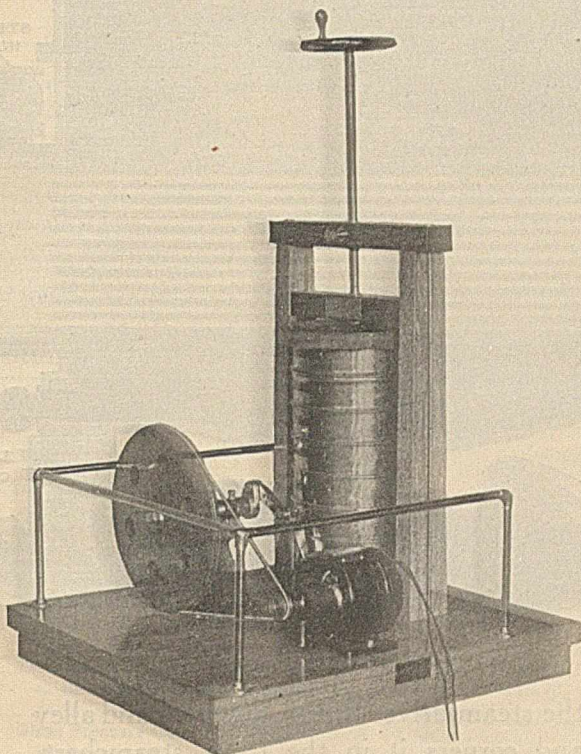
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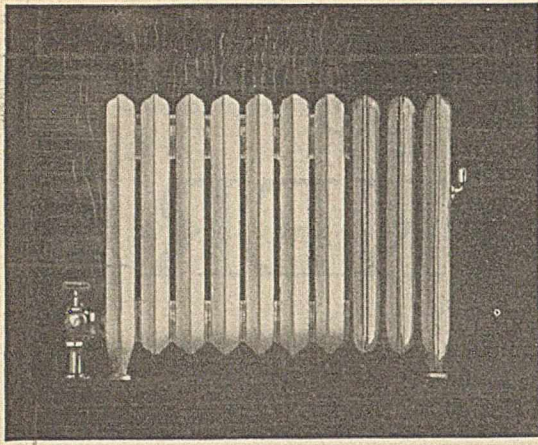
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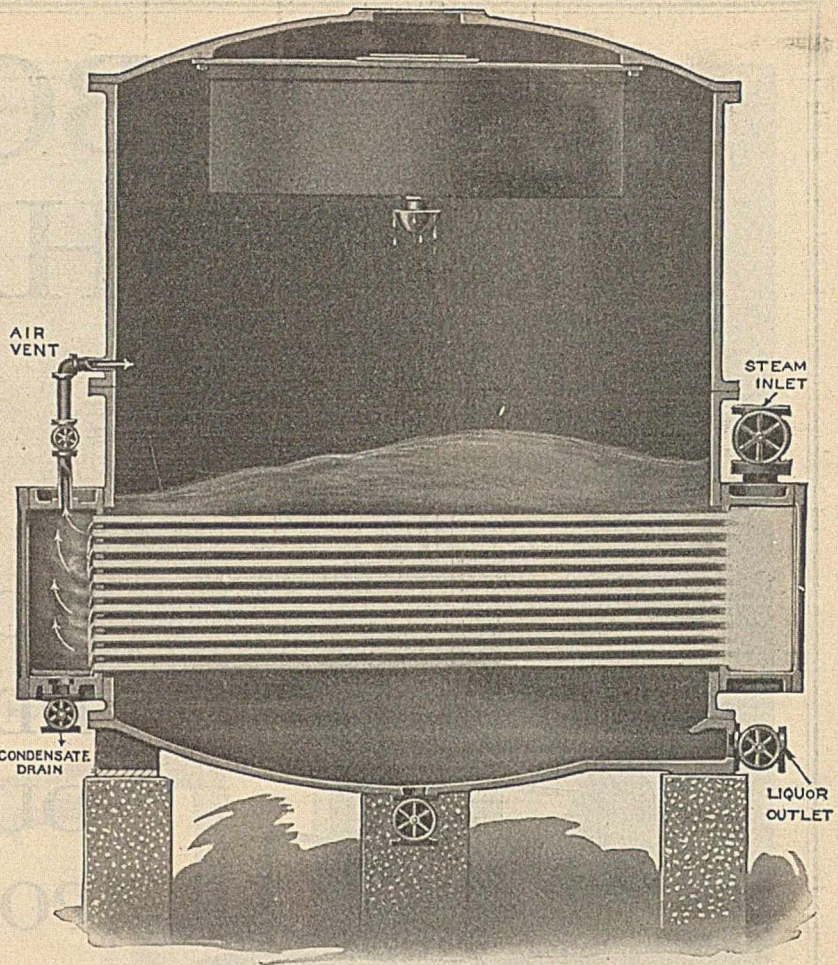


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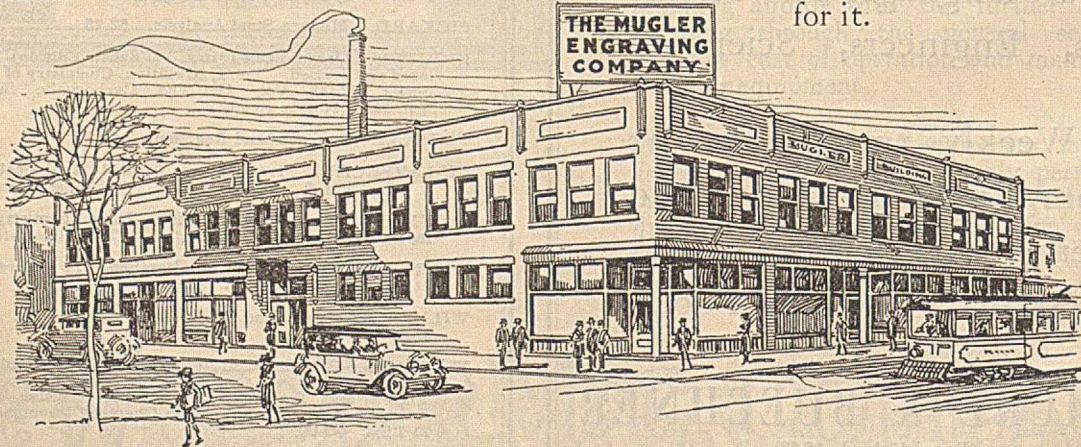
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