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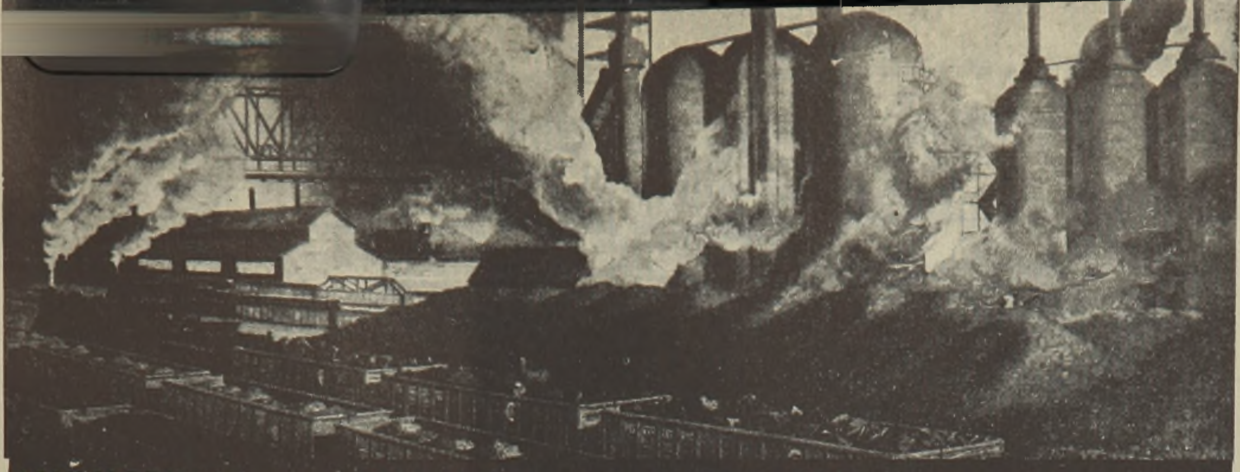

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TECHNICAL ARTICLES

FOOD QUALITY AND FLAVOR

CELLULOSE AND CELLULOSE PLASTICS

*** Indicates page number in the advertising section.**

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INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

Economics

In Defense of the Co-op. Your editors have discovered that the subject of co-ops, like politics and religion, is a highly controversial topic and if editorial serenity is to be maintained (and we insist that it should) we must revert in I. & E. C. Reports on the Chemical World Today to such relatively innocuous old reliables as cartels, power alcohol, the tariff, and the place of women in chemistry.

Comment on "Growth of Co-ops" in the January 1945 issue, page 10, brought forth hot retorts from three readers who took decided exceptions to certain statements, particularly the one that cooperative associations are exempt from the payment of federal income taxes, etc.

One critic mailed us an 8-page leaflet published by The Cooperative League (New York, Chicago, Washington) entitled "THE TRUTH about private profits and cooperative savings IS" and especially marked the following for us to read:

> **Taxation of Cooperatives**
>
> Cooperatives pay every form of taxes that private corporations do with one exception. They pay property, excise, transportation, communication, social security, unemployment, occupational, and such other taxes. *They obviously should not pay federal income taxes because cooperatives, as such, do not have incomes or profits to tax. The members of cooperatives, however, do pay personal income taxes on any savings which are returned or allocated to them, which are subject to taxation.*
>
> Any private corporation could distribute its earnings on the same basis of patronage returns on purchases and thus not have any income on which to pay taxes. Such amounts returned would be considered as a reduction in prices. . . .

Our critic No. 1 then goes on to say, and again we quote:

> The price of any article is the cost of placing it in the hands of the purchaser plus an overcharge which is the profit on that article. The Co-op returns the overcharge to the individuals who paid it. There is a difference between the controls necessary where the overcharge or profit is returned to the one who paid it and where it is disbursed to a stockholder. In the latter case the disbursement of profits bears no relation to the purchases of the products against which the profit was assessed but is based on stock holdings. The difference is fundamental and not trivial as your comment on Co-op immunity from Antitrust laws would assume.

Critics 2 and 3 submitted a joint statement which we quote in part as follows:

> It will be noted that in the example cited, the $74 paid in taxes by the private fertilizer manufacturer is out of gross margins or gross profits. In other words this $74 is not part of the cost of manufacture of fertilizer. By and large the cost to manufacture a ton of fertilizer is the same in private and cooperative factories. If after this the private manufacturer charges more than the cost of manufacture for his product, under our existing laws he must give a good share to the Government before he can pocket the difference. The Government even allows the manufacturer to set aside adequate reserves for depreciation, to spend considerable amounts for advertising, and to pay high salaries before it steps in to take a share of these profits.
>
> Let us examine how a Co-op would work. If it charges more than the cost of manufacture of fertilizer, which it ordinarily does to prevent price cutting, it is bound by the laws under which it is incorporated to return almost all of these excess charges to the consumer. On the small amount that a Co-op may retain it is bound to pay exactly the same rate of taxes as a private manufacturer.
>
> The main point is this therefore: if the private manufacturer should choose (he has a perfect right to do so) to return his overcharges to his customers he too would have no tax to pay. In other words it is not clear to us how the author of the editorial calls it unfair competition when a private manufacturer can get out of paying taxes if he chooses to return his excess profits to the customer as the Co-ops do. All the Government says is: if you choose to keep your overcharges yourselves you are taxed, be you private or cooperative enterprise. To us this seems to be fair competition.

We close this debate on the pros and cons of Co-ops in a hurry, for we read on page 7 of the little leaflet referred to previously: "because cooperatives reinforce every other institution of democracy they are always attacked and destroyed, in so far as possible, by dictators and would be dictators, who fear democracy."

We don't want to be a dictator, we are not against cooperatives; indeed, we think they have done a lot of good. We did raise a controversial question as to whether an unequal tax burden existed. Certainly, some portion, at least, of private industry thinks this is true; the proponents of Co-ops say "no". As in most controversial questions, both sides feel they have won the debate, which is desirable, for it will permit us to get on with some other phases of The Chemical World Today.

Chemical Condiments. Spices from the Orient may give way to the wizardry frequently enacted in the test tube in the hands of the chemist: Witness the rapid expansion in the demand for monosodium glutamate for flavoring soup and food. Indeed, it might be said that the chemist has in part reversed the direction of the spice

(*Continued on page 8*)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

trade. China and other parts of the Orient have been big consumers of monosodium glutamate, developing a keen taste for its flavoring qualities. United States manufacturers now are optimistic on the idea of selling the product to the American public on a large scale. Recent advertising carries the startling information that American tables will soon require a third shaker, and salt and pepper at long last will have real competition.

Manufacturers of monosodium glutamate and glutamic acid products have overcome the handicap of reduced supplies of beet sugar liquor, the raw material for their manufacture, by successfully using wheat gluten. Some producers are expected to return to beet sugar liquor as the preferred raw material as soon as conditions become normal; others may continue using wheat gluten.

Vanishing Lead Supplies. When bigger and better wars are invented, someone will have to uncover additional sources for lead. At the rate it is being presently fired upon the enemy and used up by the war industries, lead stockpiles will be a thing of the past before we get much further into 1945. The Government had a stockpile of the metal in 1943 which amounted to 273,000 tons. At the close of January the total had shrunk to 80,000 tons. The discouraging factor is that we are not providing enough lead from primary and secondary sources, and from imports, to strike a balance between consumption and supplies.

In other words, and we quote from a summary prepared by Felix E. Wormser, secretary of the Lead Industries Association, "over a million tons of lead per year *must be found* to keep the lead-consuming industries satisfied". The industry with the biggest lead appetite is the one manufacturing storage batteries. Cable covering is second, and the two together last year consumed an amount of lead (414,500 tons) which almost approximated United States mine production. Other important wartime uses are in the manufacture of tetraethyllead, lead pigments, ammunition, and bearing metals.

So serious has become the labor shortage at lead mines that United States production from this source dropped from 496,000 tons in 1942 to 446,000 tons in 1943, and to 417,000 tons in 1944. Production in 1945 from this source may not exceed 400,000 tons.

Possible methods of obtaining larger supplies would be to increase the flow from secondary or scrap lead, and to arrange for the importation of greater tonnages from Mexico and Peru. Imports of pig lead last year were 220,000 tons, and of ores and concentrates, 90,000 tons.

Both of these programs, however, face the familiar bottleneck of insufficient manpower—in the collection of old storage batteries, as well as a shortage of trained workers at smelting and refining plants. The secondary scrap reserve, says the association, is our best "lead mine". It is estimated that 500,000 tons of lead, in the form of old scrap, await collection, but that not more than 25,000 tons a month, or 300,000 tons a year, are being produced from this source.

This summary of the supply position in lead provides a fairly clear picture of the situation which (*Continued on page 10*)

forced the WPB to curtail drastically the use of the metal by such essential consuming fields as pigments, colors, and chemicals. The table shows importance of these requirements:

ESTIMATED CONSUMPTION OF LEAD[a]
(Including antimonial lead)

	Short Tons	
	In Peace *1940*	In War *1944*
White lead	65,500	67,500
Tetraethyllead	44,000	84,000
Red lead and litharge[b]	59,400	85,000
Storage batteries	220,200	292,500
Cable covering	107,400	122,000
Building[c]	65,000	74,000
Automobiles	11,000	7,500
Ammunition[d]	56,000	47,500
Coatings	6,000	5,500
Foil	23,500	15,000
Bearing metals	14,000	38,500
Solder	24,000	36,500
Type metal	16,800	22,000
Calking	19,200	33,000
Other uses	50,000	130,000[e]
	782,000	1,060,500

[a] American Bureau Metal Statistics and Lead Industries Assoc.
[b] Exclusive of oxides for storage batteries.
[c] Includes lead used in chemical construction.
[d] Small arms ammunition consumed a total of 178,000 tons in 1943.
[e] Includes antimonial lead products, collapsible tubes, basic lead sulfate, steel and wire, brass, other miscellaneous uses.

In the instance of white lead paints, the replacement materials in some cases are even more difficult to locate than lead. Manpower and production difficulties have to be contended with in titanium and zinc pigments. Motorists by this time have also learned that there are no practical substitutes for tetraethyllead as antiknock ingredients in gasoline.

As much as 80,000 tons of lead were consumed last year in the manufacture of tetraethyllead, and as the great bulk of the latter is now entering military fuels, there is little likelihood that supplies of lead will be curtailed for this purpose. During 1945, according to the industry, even larger tonnages of the metal will be needed by the tetraethyllead plants. The antiknock ingredient is made by heating ethyl chloride under pressure with sodium-lead alloy.

Civilian motor cars will probably receive little or no antiknock gasoline while the war lasts, unless some other negative catalysts for engine detonation are developed. For many automobile power plants that is not exactly a good thing, and C. F. Kettering has pointed out that engine knock is a barrier to high power and efficiency. The high-compression ratios of present-day engines demand fuels with antiknock characteristics. They are constructed, says Kettering, of "metals and brains", but even this combination cannot overcome the absence of so great an efficiency factor as tetraethyllead.

Nematode Nemesis. DD, first reported in these columns just a year ago (February 1944, advertising page 5) is being successfully used to clear the soil of the sugar beet nematode. DD is a mixture of 1.3-dichloropropylene and 1,2-dichloropropane, and the U. S. Department of Agriculture has been carrying out experiments in the California area on its ability to kill off this pest. The chemicals are applied in emulsion form to the infested ground, dikes being erected to keep the solution in bounds. For complete elimination of the nematode, about 600 pounds of the emulsion are needed per acre. Projected uses cover the fumigation of greenhouse soil for the control of the many common pests that bedevil the professional nursery man.

(*Continued on page 14*)

I. & E. C. Reports on the Chemical World Today

Technology

The Future in Meat By-Products. Stopping to realize that nearly every individual eats meat and that the average American pays more for meat than for gasoline, it can be appreciated that meat and meat products constitute one of the largest industries in the country today. But without by-products, this great industry could not exist in its present form. It operates on such a small margin of profit that the by-products, which actually amount to an industry within an industry, are an important factor, and in fact, the future of the meat industry depends on them.

A factor in the meat industry which makes the utilization of by-products so attractive to industrial development is its concentration in relatively few locations. This value of location constitutes an advantage beyond the intrinsic value of the by-products themselves. Costly factors of collection and transportation do not enter in because the by-products are available in sufficient quantities for economical processing on the spot. Such concentration is frequently a determining factor in the utilization of a by-product, but it is not specific to the animal by-product industry. For example, we have the same thing in the by-product coke and the oil industries.

This very concentration of the meat industry into a few huge operations made the disposal of waste a serious problem, and the mere fact that it had to be solved without dumping or stream pollution led to the complete utilization of by-products that features the industry today. By-products of meat have always been important—witness the prehistoric use of hides, bone, and hair—but it is only recently that they have begun to receive the attention of scientific development and exploitation. There has been a great acceleration of interest in this direction during the past 10 to 25 years.

Once the solution to the problem of waste disposal, fertilizer outlets claim very little from the packing house today. Enzyme and glandular materials go into biologicals; high-grade fatty materials are frequently used in the production of soap and glycerol; low-grade protein materials are used for feeder tankage; but as scientific development has shown more valuable uses for these materials, their utilization has constantly been diverted into more economically important channels. Hence we see present developments in utilizing low-grade protein materials for synthesizing amino acid derivatives and in using low-grade fats for making fatty acid derivatives—nitriles, amides, and others.

It is this constant up-grading of by-products under the impact of research wherein lies its tremendous future, for it has a great future, according to authorities in the field. The future of the meat by-products industry may be considered to lie either in the synthesis of new materials or in the extraction of valuable biologicals. Both are important factors today. Notable among recent developments in synthesis are the fine chemicals derived from fats and the fatty acids. They are finding applications as flotation agents, wetting agents, detergents, and hundreds of other uses where fats or fatty acids would be useless. High molecular weight amines are obtained entirely from fats, of both vegetable and animal origin, and entire new fields are being opened up to these compounds.

Physiologically active materials constitute an important animal by-product. Without insulin, many more people would be dead of diabetes. Liver concentrates permit the treatment of anemia where the administration of equivalent volumes of liver itself would be impossible. High potency glandular extracts are increasingly important, and as a source for them, meat by-products will continue to be important for a long time to come. With the amount of work currently being done on glandular products now obtained from animals, it is to be expected that they will eventually be synthesized. But since in many cases we do not know their structure nor the way in which they function, their replacement by synthetic products seems to be distinctly far in the future.

(*Continued on page 18*)

Proteins have so many interesting and unusual properties that the field is virtually unexplored. If, for instance, the keratins from hair and hoofs could be sheeted, many interesting uses could be found for them, but this would require a change of phase without chemical alteration, which has been the obstacle in the past. Proteins are the subject of intense activity today, claiming the attention not only of chemists but of histologists in the study of tissues. Most of this work is being conducted under the cloak of military secrecy.

Tying into the picture on the future of meat by-products is their national significance as an agricultural raw material, an ever renewable resource in contrast to our mineral resources that are fast being depleted. But this is a problem that goes far and beyond the responsibility of any one industry. The over-all prosperity of agriculture will increase as new outlets are developed for agricultural products. The Government has become cognizant of this as indicated by the establishment of regional research laboratories. Up until that time, all effort had been directed toward showing the farmer how he could produce more, how he could get more out of his land, but very little interest was shown in the development of new channels for the absorption of these increased productions.

The consumption of foods probably would not be increased by making them better. True, if such an economic condition should be established in this country so that everybody had enough to eat and if all our population could afford a proper diet, then the total over-all production of food would be increased. But most efforts in the direction of increasing the consumption of food are of a competitive nature, tending to increase the sales of a certain type or brand of food at the expense of some other, total consumption remaining about the same. The very large increased use of farm products will be in nonedible directions; not in expansion of food uses. A move in this direction is the creation of synthetic chemicals from agricultural products, but it has only been within comparatively recent years that there have been strenuous efforts along this line.

It has been stated by individuals who should know the various ramifications of research that no industry has greater potentialities than the meat by-products industry, nor so many problems on which so little is being done. Both statements we think can be challenged, but they do make us stop and think! Presenting virgin territory for scientific research in which the surface has not even been scratched, meat by-products will develop major industries in the not too distant future.

(*Continued on page 22*)

I. & E. C. Reports on the Chemical World Today

Technology

Milkweed Floss. Some new products are developed and make their way because of special properties and applications in which they perform new functions. Others get their start when materials which they can replace become temporarily unavailable. Among the many products of this latter type is milkweed floss, now being used as a substitute for kapok in life preservers. Its continuance as an industrial product after the present emergency, however, may require the support of by-products which as yet are not fully developed.

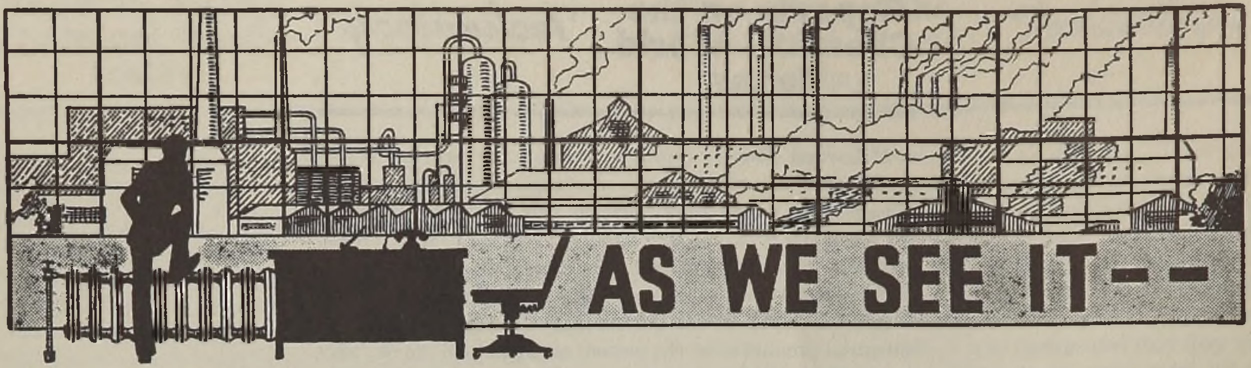
The production of milkweed floss in this country is confined to a single operation at Petoskey, Mich. Built in 1943 by the Defense Plant Corporation and operated by the Milkweed Floss Corporation of America, the plant has a weekly output of 50,000 pounds which goes entirely into life preservers. Postwar possibilities for milkweed floss include upholstery, pillows, and insulating material, for which it is claimed to have many advantages. In these uses it will compete with kapok, and advantages such as mechanical harvesting and treatment of the floss to reduce dusting may make it more desirable than kapok.

Many possible uses have been promised for milkweed products, amounting to total utilization of the plant if carried to the extreme. Work at Polytechnic Institute of Brooklyn has demonstrated the semidrying properties of milkweed seed oil and its potential value in protective coatings [Industrial and Engineering Chemistry, 37, 179–81 (1945)], and pilot-plant work on the extraction and development of the oil is under way at Iowa State College, Ames, Iowa. Other by-products include paper from the stalk, based on work done at the Institute of Paper Chemistry, Appleton, Wis., latex and chlorophyll from the leaves, and wax and furfural from the shells.

A big factor in the future industrial development of milkweed is its adaptation as a cultivated crop. At the present time, all floss is coming from pods gathered from the wild-growing plants. Collections in 1944 by individual farmers through the War Hemp Industry, an agency of the Commodity Credit Corporation, amounted to 2,500,000 bags of pods, 10 pounds each, green weight. This represents 2,000,000 pounds of floss. Some milkweed is being cultivated near Petoskey but only for experimental purposes.

Claims are made that the deep-root system of the milkweed plant makes it valuable in soil conservation. Added to this are its moisture-retaining properties that should permit it to be grown in comparatively dry regions, but varieties growing in the northern lake states have been shown to be best suited to industrial use.

The slow maturing season in this district overcomes the problem of losses through rapid opening of the pods encountered in the warmer climates. Work is now being directed toward milkweed cultivation in several of the government agricultural experiment stations with an eye toward its development as a crop for submarginal lands. The postwar industrial position of milkweed, only a part of which is now being utilized, will depend both on its establishment as a crop and the degree to which the utilization of its several parts will become economically feasible.



AS WE SEE IT--

This Month

FOOD, its quality and flavor, starts the March issue in a tasty way. Four articles form a symposium on the subject and are a tribute to Harvey W. Wiley and they come from the memorial symposium to him held by the Division of Agriculture and Food Chemistry during the recent North Jersey Meeting.

Harvey W. Wiley, as one will find in reading the articles, is the father of the pure food and drug legislation and as such gave great impetus to the scientific control of food in all its aspects. Thus Ernest C. Thompson of the Borden Company in his article on quality control in the dairy industry states that Wiley's "sound basic principles of quality control as related in particular to adulteration and the use of preservatives opened the way to recognizing that all foods should be pure and clean, that their keeping qualities should not rest upon the use of preservatives". Thompson then proceeds to describe the practical results of two prominent accomplishments in dairy products quality control—removal of diseased cattle from milk producing herds, and the education and supervision of personnel. He states that since 1917, the number of cattle showing positive reactions to tuberculin tests has decreased from 3.2% to 0.7%.

An old art is slowly yielding to the organizing power of chemistry and E. C. Crocker of Arthur D. Little, Inc., points the way in his study of the volatile constituents of food flavors. He treats flavoring materials as organic chemicals possessing vapor pressures, boiling points, and other characteristic properties. In his article there is a table of 240 typical flavors arranged in 14 classes according to vapor pressures. The range in volatility from group to group ranges not more than two to one yet over the 14 groups the variation in vapor pressure is some three thousand fold—from one millimeter to less than one-thousandth of a millimeter. Suggestions for the use of the table are included.

Number three of the Wiley symposium is from H. E. Robinson and H. C. Black, Swift and Company, on flavors in food fats. The quantity of food fats used in our diet is not appreciated, say the authors, and the number of these materials they list is impressive. The authors delve into the chemical facts behind flavors in fats, and explain some of the things that happen to an oil before it gets to your table.

Quality in meat and meat products may seem quite theoretical during the present shortage but O. G. Hankins of the U. S. Department of Agriculture has much to say about the subject. Many factors beginning at the life of the animal right down through the final processing effect the quality of the meat.

A second symposium on cellulose and cellulose plastics brings six papers to our readers. Recent progress in the field is the subject of the first paper by three authors from Polytechnic Institute of Brooklyn. Weather resistance of cellulose ester plastic compounds is reported by L. W. A. Meyer and W. M. Gearhart of the Tennessee Eastman Corporation. They report on the appearance and physical properties of a number of cellulose acetate butyrate and cellulose acetate plastics that were exposed for two years to the weather in Arizona, Florida, and Tennessee. They found that resistance to weathering is improved somewhat by the proper choice of plasticizer but the major improvement came by adding small amounts of an ultraviolet light inhibitor such as phenyl salicylate.

The temperature of the injection cylinder is the most important variable on tensile and impact values of cellulose plastics according to R. H. Ball, C. E. Leyes, and A. A. Melnychuk of the Celanese Corporation of America. In their article on cellulosic molding compounds, the authors state that an increased injection cylinder temperature gives greater impact strength, reduces tensile strength, and increases elongation at the break point.

Two important papers for the agricultural and fertilizer field follow in this issue. The first is by Shaw, Parker, and Ezekiel, the second by Mehring. All authors are with the U. S. Department of Agriculture. The first paper comes to the conclusion that the percentage of nitrogen in fertilizer is a ratio between the prices of nitrogen and phosphate and potash. They also conclude that a drop of 20% in nitrogen price plus a corresponding increase of 20% in plant-food content would have meant, on a 1937 basis, over a million tons of additional fertilizer for farmers with no increase in expenditure.

Mehring in his article places the gradual rise of nitrogen consumption and states that the factors effecting fertilizer nitrogen consumption are cash, farm income, and cost per unit of nitrogen in various competing forms. He also says that consumption of plant nutrients including nitrogen is increasing independent of farm income or price and not the least factor affecting this increase is education and sales promotion.

Next Month

APRIL will be featured by an extensive symposium of six papers on catalysts and catalytic methods in the petroleum field. The subject is greatly important to our present war effort and to the future welfare of our country, for the chemist is responsible for the fuels to power our machines. No single technique holds more promise than that of catalytic chemistry and we are planning much on that subject for next month.

The meeting of two new arts will be seen in an article "Emulsion Polymerization of Acrylic Esters" with the newer synthetic detergents.

Cholesterol can be separated from degras by solvent extraction as we will see next month, along with other articles on the production of hydrogen sulfide from sulfur and hydrocarbon and an article on red lead-alkyd resin reaction.

Orange juice is still giving a lot of trouble when it comes to canning commercially but chemistry is still working on the problem as we shall see when April comes around. Then too we shall have something on acetylation of castor oil, the effect of humidity on synthetic rubber, and a study on naphthene pyrolysis for producing butadiene.

And that is As We See It.

F. S. Van Antwerpen

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials
WALTER J. MURPHY, EDITOR

Civil Service Snubs the Chemist

SECTION 5 of the Veterans' Preference Act of 1944 contains the following statement:

> No minimum educational requirement will be prescribed in any civil-service examination except for such scientific, technical, or professional positions the duties of which the Civil Service Commission decides cannot be performed by a person who does not have such education. The Commission shall make a part of its public records its reasons for such decision.

According to the new law, the responsibility rests squarely with the Civil Service Commission to decide if minimum educational qualifications are to be required for positions of a scientific, technical, or professional nature and if so, the Commission must state publicly its reason or reasons for such action.

The American Chemical Society is informed that the Civil Service commission will require minimum educational qualifications in the case of medical doctors, dentists, veterinarians, teachers, nurses, and some other classifications which very obviously fall within the category of scientific, technical, and professional positions, but will not demand minimum educational requirements from those who seek positions as chemists, physicists, and engineers. Apparently it is now the considered judgment of the Civil Service commission that chemists need not be given a formal and organized education.

The Directors of the American Chemical Society at their December meeting in Washington instructed the Secretary of the Society to protest to the commission against such a policy. Secretary Parsons in his letter to the commission pointed out that it is as easy to convert a nurse's aide into a surgeon by practical experience, as it is to develop a chemist from a technician without resort to chemical education.

It is well that the 40,000-odd members of the Society and, indeed, all the chemists of the country be informed of the disservice to their profession that comes from the present stand of the Civil Service Commission. It is well for the country at large to know that the Government will find it increasingly difficult to continue extensive research programs for the simple reason that chemists in large numbers will and should decide against government service when they discover that the commission does not consider chemists worthy of professional recognition, while readily affording such recognition to doctors, dentists, veterinarians, and nurses.

The chemical profession resents the discriminatory action of the commission. Under such adverse treatment, will it be at all surprising to find the really competent chemists turning to industry rather than to government service when looking for positions in the postwar period? Perhaps the commission is ignorant of the fact that the demand for chemists and chemical engineers in the postwar era will greatly exceed the supply.

The commission, we are told, seeks to defend its action on chemists by pointing out that examinations will screen out the incompetent. In our opinion this is no answer to the question raised by Charles L. Parsons in his letter to the commission.

The question simply is, will the commission recognize the chemist as a professional in the same way as it does the doctor, the dentist, the nurse, etc., or has it concluded that it can safely place him in a very much inferior place in the educational scale and get away with it? Because we can visualize the threat to the future of government research projects in the present stand of the commission, we earnestly suggest that it immediately reverse itself on this matter.

The Crisis in Higher Education

MEMBERS of the Committee on Education of the House of Representatives are now actively engaged in studying a 74-page report prepared by Francis J. Brown, director of the American Council on Education, Dean Herluf V. Olsen, Amos Tuck School of Business Administration, and an advisory committee of twelve representatives of higher education, headed by Cloyd H. Marvin, president of George Washington University, discussing the critical status of higher education in this country.

Unless relief of several kinds, including substantial financial aid, is provided by Congress not later than July 1, 1945, this committee sees nothing ahead but deficit financing, inadequate staffs and equipment, and a general weakening of the colleges and universities with the country the ultimate sufferer. To correct these conditions, the advisory committee has made a number of specific recommendations, several of a strictly financial character designed to provide as much as 25 million dollars annually in federal aid.

In condensed form a few of the other proposals are:

> That the Selective Service System at the earliest possible time re-establish student deferment for those majoring in studies essential to the national welfare. And that Congress, in writing national service legislation, make similar provisions.
>
> That the War and Navy Departments include in their basis for

> discharge consideration of the educational plans of students who have completed two or more years of college work in essential fields and who will continue their education.
>
> That faculty members teaching in essential fields be deferred to meet the educational needs of veterans and others and that Congress, in writing national service legislation, consider those teaching in necessary fields as being engaged in an essential activity.
>
> That members of faculties of higher educational institutions whose services are requested by the institutions be given priority in release from military or other government positions.

To readers of INDUSTRIAL AND ENGINEERING CHEMISTRY these four suggestions have a very familiar sound. It is nice to feel that no longer are we "a voice crying in the wilderness".

Particularly pertinent are the concluding remarks of the committee:

> Serious as this situation may be from the standpoint of individual institutions, it may develop into a national crisis by drying up certain of the sources from which streams of mental power have flowed into every phase of our common life throughout the years and during the present war.
>
> Furthermore, we cannot ignore the fact that returning veterans, both now and after the close of the war, will expect to find colleges and universities available from which they can secure the education which the Government has generously provided for and which they need for peacetime pursuits. In addition, America will turn to its institutions of higher education to furnish broad understanding of economic, social, and international matters in order to meet the complex problems of the postwar world.

Personally, we feel that the committee understates the facts when it says a national crisis may develop. In our opinion that crisis is with us right now. Unless these senseless and dangerous conditions are removed immediately, the future of America will be jeopardized by a handful of men who are leading us up a blind alley. Technologically, we will be greatly inferior to other nations. That is, indeed, a sad picture to contemplate when it could and should be just the opposite.

Defining Chemotherapy

RECENTLY one of the leading life insurance companies of the country devoted full-page advertising in national publications to educating John Q. Public, Mrs. Public, and all the little Publics on the meaning of that strange new word "chemotherapy".

In vain did we search this advertisement for the titles "chemist" and "chemical engineer", but we did read the following:

> The next discovery, penicillin, although not strictly a chemical, attacks some of the same germs as the sulfa drugs—and others against which these drugs have little or no success. But the search for other "specific "chemicals is far from over. *Medical scientists* (the italics are ours) constantly seek to improve existing ones and find new germ-fighting elements. . . But chemotherapy, rightly used, is a tremendous gift of medical science to our civilization.

In behalf of the chemists who have discovered hundreds of chemicals with therapeutic value, we protest against the use of the meaningless term "medical scientists".

To John Q. Public, his wife, and their progeny, that term means but one thing—the doctor, the physician. This is palpably unfair to the research chemists who have developed chemicals for the medical profession to prescribe and use; it is unfair to the chemical engineers who have taken the new chemicals with therapeutic value developed by research chemists and by the application of chemical engineering principles have made the sulfa drugs, penicillin, vitamins, and other chemicals available to the medical profession in large quantities at relatively low cost. Very decidedly these researchers and production geniuses want to be known to the public as chemists and chemical engineers and certainly not as medical scientists.

In calling attention to this slight to the members of the chemical profession, it is not our intention to minimize or play down in any way the medical profession. There is plenty of glory for all the professions cooperating so effectively in conquering, or at least lessening, the effects of the common diseases that afflict mankind. All the more reason, then, that each should be given proper credit and in terms that are certain not to lead to misunderstanding on the part of the lay public.

Teamwork on Publicity

A FEW months ago we asked for more active support from our membership in furthering certain work of the AMERICAN CHEMICAL SOCIETY News Service. We are delighted to report widespread cooperation. It has been highly effective in getting before the lay public the logical position of the SOCIETY on such vital matters as deferment of chemists and chemical engineers and the necessity, even in wartime, of maintaining adequate numbers of bona fide students in our scientific courses.

Space available will not permit mention of all such cooperation which has been brought to our attention. John H. Yoe, of the University of Virginia, forwarded his copy of "Only God and a Few Humans Know" to the editor of the *Richmond Times-Dispatch*. The practical result of this action was a stirring editorial in that leading Southern daily on February 14 under the title "The Crisis in Science". Another SOCIETY member, Arthur F. Scott, acting president of Reed College, Portland, Oregon, arranged for the publication of the I. & E. C. editorial of last December entitled "Science Is Power" in the *Portland Journal* as a guest editorial.

Enlightened and informed public opinion will, indeed, have a noticeable effect on the thinking of certain Washington officialdom. Witness the rather belated recognition of technical, scientific, and research personnel in the most recent Selective Service rules on occupational deferments. This is, however, but a start. If the forty-odd thousand members of this SOCIETY and members of other scientific groups would, as individuals, put their shoulders to the wheel, so to speak, it might yet be possible to drive home to those in charge the serious consequences that inevitably will follow the present procedure of stripping our colleges of students in science courses in order to add a few divisions to our Armed Forces. It is even possible that the Mead Committee (new name for the old and generally respected Truman Committee), influenced by expressions of opinion in our newspapers and magazines, might decide that the subject was one that should be investigated.

Is Cooperation the Proper Name?

THE Antitrust Division of the Department of Justice recently has sent letters to a large number of companies requesting, or perhaps merely suggesting, that they supply the division with copies of patent license agreements to which they are parties. In some instances, so we are advised, requests are made for copies of license agreements to which they have been a party and which have been cancelled subsequent to a specified date. The contracts are supposed to be used in connection with a study of patent licensing practices conducted by the Antitrust Division, and the request for copies of these contracts does not imply that a violation of the antitrust laws is necessarily involved.

The division stresses that compliance with these requests is purely voluntary and that no company is under compulsion to supply copies of its patent license agreements until subpoenaed.

It seems to us, however, that no one should voluntarily divulge the contents of license agreements without first securing the consent of the other party or parties to these agreements. For the Antitrust Division to request such a disclosure without giving the party who is asked to divulge confidential information the protection of a subpoena, in case the other parties to the agreement raise objection, puts the companies which decide to comply with the request and do cooperate in these studies at a legal disadvantage.

If individuals or concerns do not voluntarily supply copies of their patent license agreements as requested, probably they will be put down as uncooperative with the Antitrust Division, and, if they supply the copies without a subpoena, they may justifiably receive complaints from the other parties to these agreements that private information was disclosed without proper consent.

Should not the Antitrust Division at least advise companies which comply with its request as to just what protection the division is prepared to give cooperating companies in case complaints are made to them by the other parties to these license agreements?

As we watch developments here in the Nation's capital, we sometimes find ourselves wondering to just what lengths the American people are prepared to go in allowing the basic concepts of Anglo-Saxon jurisprudence to be changed. As school children we were told that American law was based on the premises (1) that a man is presumed to be innocent until definitely proved to be guilty; (2) that the burden of the proof rests on the accuser, not the accused; and (3) that the accused must be judged by a group of his peers.

Is it no longer possible to write our laws so that the reasonably intelligent can understand them—can tell what is lawful, and what is not?

Are we reaching the point where we are "suspect" if we do not invite the corner policeman in to inspect our home every Saturday night, or fail to welcome him with open arms at any time of the day or night that he chooses to select to snoop around?

Are we as a people ready to scrap completely our Magna Charta heritage and the Bill of Rights in favor of the Continental European idea that every individual is *always suspect?*

Are we reaching the point where we must submit all our actions to the scrutiny of a prosecuting group or groups, or be considered uncooperative and probably guilty of some evil doing?

The recent request of the Antitrust Division for copies of license agreements may appear to those who have every confidence in the propriety of such agreements as just another inquiry from a governmental agency.

To us, however, it appears to be an impertinence!

Chemistry via the Radio

CONGRATULATIONS to the United States Rubber Company on its radio program over C.B.S. Sunday afternoons at 3 P.M., featuring the New York Philharmonic Symphony and a series of short discussions by well-known scientists.

The subject of chemistry and chemists and chemical engineers is receiving full recognition by those arranging the programs. Three notables of the chemical profession already have appeared: Irving Langmuir, Robert E. Wilson, and Vincent du Vigneaud. Roger Adams, Chairman of the Board of Directors of the AMERICAN CHEMICAL SOCIETY, is scheduled to speak later in the series.

We commend the United States Rubber Company for its foresight in making it possible for scientists to be heard on the air telling the lay public not only something authoritative about the achievements of science, but something about the problems of scientists and their relationship to their nontechnical fellow beings.

Personalized Credit for the Chemist

AGAIN and again on these editorial pages we have stressed the desirability of personalized credit for outstanding research achievements when possible.

It was particularly encouraging, therefore, to pick up a Washington newspaper a week or so ago which showed an Associated Press wirephoto of Raymond L. Libby, of the Cyanamid Research Laboratories, Stamford, Conn., discoverer of a method of making penicillin pills. In one respect the story could have been improved—it did not define Libby as a chemist and an ACS member.

FOOD QUALITY AND FLAVOR

Good Housekeeping

MAGAZINE

Dr Wiley's *first article on* Pure Food

This excellent likeness of Harvey W. Wiley appeared on the front cover of *Good Housekeeping* for May, 1912. We are pleased to reproduce it here with the kind permission of that magazine.

QUALITY CONTROL IN THE DAIRY INDUSTRY

Ernest C. Thompson

THE BORDEN COMPANY, 350 MADISON AVENUE
NEW YORK 17, N. Y.

QUALITY and quality control in dairy products involve extensive considerations. They encompass various fields of scientific and technological activities. In this limited paper it is possible to discuss only partially and briefly this broad and complex subject of great importance to the dairy industry. It is opportune to recall briefly Harvey W. Wiley's direct and indirect influence on the approach of the dairy industry to the important responsibility of quality and quality control. One of his first problems upon becoming chief of the Chemical Division, Department of Agriculture, in 1883 was the more extensive study of food adulteration. He immediately organized a section for the specific study of food adulteration and continued unceasingly in his efforts to place before the public the danger of such adulteration and to secure legislation for its prohibition. When the Food and Drug Law was finally enacted in 1906, it was, with but slight variation, in the form originally drafted by Wiley, and thus he may be regarded as the father of pure food and drug legislation in the United States.

Wiley continued as chief of the Bureau until 1911 when he retired. He was specially emphatic in his protestations against any form of adulteration or the use of chemical preservatives in food products. During those years adulteration and chemical preservation were practiced to a limited extent by the food industry. The use of preservatives was occasionally detected in dairy products. Milk, however, did not lend itself readily to extensive adulteration, but was limited mainly to skimming and the addition of water. Wiley and his associates vigorously campaigned against such practices. His sound basic principles of quality control as related in particular to adulteration and the use of preservatives pointed the way to recognizing that all foods should be pure

The four papers which follow were presented as part of the

HARVEY W. WILEY MEMORIAL SYMPOSIUM

before the Division of Agricultural and Food Chemistry at the 108th Meeting of the American Chemical Society, New York, N. Y.

and clean, that their keeping qualities should not rest upon the use of preservatives. The dairy industry, as part of the great food industry, joins in acknowledging Harvey W. Wiley as an outstanding leader and public servant whose staunch adherence to fundamental principles has had a far-reaching beneficial effect.

A SAFE MILK SUPPLY

Two prominent accomplishments in quality control stand out in the dairy field today—first, the removal of diseased cattle from milk-producing herds, and second, the education and supervision of personnel in the interest of eliminating individuals who may be suffering with infectious, contagious, or communicable diseases. This work has been done so well that consumers are practically unaware now that a danger of this nature ever existed.

Between 1850 and 1910 it was recognized that milk might become the vehicle for the transmission of pathogenic organisms which might endanger human life. Cattle are subject to bovine tuberculosis, brucellosis or undulant fever, Bang's disease (responsible for contagious abortion), foot and mouth disease, and other diseases infectious to man. Fortunately none have been highly prevalent in the milk-producing herds in the United States with the exception of bovine tuberculosis. In 1910 it was estimated that 10% of the dairy cattle in the United States would react positively to the tuberculin test. In that year the Division of Animal Industry of the United States Department of Agriculture began a series of tests and examinations looking toward the elimination of such infected animals. Reports showed in 1917 that, of 20,101 cattle tested, 3.2% reacted to the tests; in 1922, of 2,384,235 cattle tested, 2.5% reacted; and in 1936, of 22,918,038 cattle tested, 0.7% reacted. In other words, over a period of twenty years, positive reactions of cattle tested decreased from 3.2 to 0.7% even though the number of cattle tested increased a thousand fold. Mastitis is the general term for the bacterial invasion of udder tissue. The udder becomes inflamed and the composition of the milk is altered. Inasmuch as a mixed bacterial flora may be present, the presence of pathogens may exist. Mastitis is readily recognized, and cattle showing any abnormality with respect to the appearance of the udder or milk obtained therefrom is considered as justification for their separation from the herd and the rejection of all such milk as unfit for human consumption. It was estimated that farmers lost 3% of their potential milk production due to mastitis in 1942. Recent studies indicate that sulfa drugs are highly effective in the destruction of all bacterial types associated with mastitis. The outlook is bright for the further reduction of mastitis in cattle. A healthy cow is a prime requisite to safe milk. It is unquestionable that today we have more healthy cattle in milk-producing herds than any nation in the world, and the dairy industry is organized to maintain the necessary control continuously. The farmer has learned from experience the vital significance of any diseased cattle in the herd; frequent inspections have stimulated his vigilance, and the enforcement of rigid regulations has led him to realize that only healthy cattle pay dividends.

Anyone intimately connected with the production or handling of milk should have good health and clean habits. Certain of the serious epidemic diseases such as typhoid fever, paratyphoid fever, streptococcus sore throat, scarlet fever, diphtheria, and dysentery may be carried through milk should it become contaminated as a result of unsanitary handling. This presented a serious problem some fifty years ago.

For a number of years health officials throughout the nation have given continuous attention to bettering sanitary conditions on dairy farms, eliminating diseased cattle, encouraging clean milk production, proper pasteurization, and careful supervision over the health of employees. As a result the problem of a safe milk supply no longer exists. The adoption of pasteurization by milk distributors and those manufacturing dairy products has further guaranteed the safety of the milk supply. More recently the phosphatase test has furnished a control method for determining the thoroughness of pasteurization.

A CLEAN MILK SUPPLY

Not only must the production of milk be clean but it must be maintained in clean condition from the moment it is drawn from the cow until delivery to the consumer, irrespective of what form it assumes or the type of package that serves as the container.

A clean milk supply means one in which the milk is free from visible dirt and has a low bacterial count. As far as market milk, cream, and closely related products are concerned, state and local boards of health have promulgated detailed regulations for every phase of sanitation connected with the maintenance of clean healthy cows, proper construction of barns, use of small mouthed milk pails, milking and handling of milk by healthy personnel, use of clean and sterilized utensils, proper use and care of milking

Harvey W. Wiley's important influence on the most important activity of the dairy industry—quality and quality control—is reviewed. What constitutes a safe and clean milk supply? Important considerations in sanitation are discussed in connection with the phenomenal growth of the dairy industry. Composition and consumer-acceptance factors are presented for the major milk products—milk and cream, butter, ice cream, cheese, evaporated and condensed milks, nonfat dry milk solids, and dry whole milk. Quality control is shown in the fields of standardization, fortification, and nutrition.

machines, prompt and efficient cooling of the milk, and prompt delivery of the milk to its destination. These regulations have included every phase of factory sanitation and have provided for regular and continuous factory inspections. To assist local health officers of smaller communities and serve as a guide to public health officials, the United States Public Health Service has made available through the years a Milk Ordinance Code outlining the minimum requirements of a safe and clean milk supply. Where milk is produced for manufacturing purposes and does not come under the direct supervision of local boards of health, there is a growing tendency toward the adoption of those standards which are recognized as satisfactory for market milk.

The American Dry Milk Institute, representing the majority of nonfat dry-milk solids manufacturers, and the Evaporated Milk Association, representing the evaporated milk industry, have developed their own Sanitary and Quality Standards. These include the requirements of a clean milk supply and the maintenance of strict factory sanitation based on the established and recognized requirements for market milk.

Section 402 of the new Federal Food, Drug and Cosmetic Act states that a food shall be deemed to be adulterated if it has been prepared, packed, or held under unsanitary conditions whereby it may have become contaminated with filth or whereby it may have been rendered injurious to health. This requirement is mandatory to all producers of milk and milk products which enter interstate commerce, and its effect is far-reaching.

SANITATION

Each can of milk is customarily examined at the receiving station immediately as to temperature, off-odor, off-flavor, and, if necessary, acidity and sediment. These tests are to determine, as far as possible, whether the milk meets established requirements. In addition, all dairies are under constant inspection, and periodic determinations for sediment and bacterial quality are made to ensure a continuously clean milk supply.

Equal in importance to a clean milk supply is the prevention of contamination during processing. Bacteriological cleanliness in contrast to apparent cleanliness is necessary. Thorough washing and cleaning of all equipment immediately after use is important. Alkaline washing compounds such as trisodium phosphate and sodium hydroxide, carbonate, or metasilicate are used separately or in various combinations. More recently organic acids, formerly considered objectionable on account of their corrosive action, are being used in combination with surface-active agents and corrosive retarders. Their inherent inhibiting effects on objectionable microorganisms give promise of further improvement in the sanitary practices of the industry. Steam sterilization is used whenever possible; otherwise hypochlorite solutions of tested strength of 50 to 250 p.p.m. available chlorine are applied. Bacteriological surveys are made just prior to or during operations where there is evidence of unusual contamination. Water supplies are constantly checked.

METHODS OF EXAMINATION

Bacteriological methods used for the examination of raw milk supplies and the determination of sediment are published in the 8th revised edition of Standard Methods for the Examination of Dairy Products of the American Public Health Association. These methods are the standard plate count, the direct microscopic method, and the methylene blue reduction method.

With the development of efficient single-service strainers for dairy farms and of efficient strainers, clarifiers, and filters for milk-receiving plants, the sediment test is becoming more and more a measure of the efficiency of these sediment-removing devices. The sediment test, which is the measure of visible dirt, compares the sediment disk with photographic standards. Until 1939 the photographic standards were designed for measuring sediment on stirred samples of milk. Since that time there has been a growing tendency to develop standards for sediment when the samples are withdrawn from the bottom of the can without stirring. This procedure is more favorable to recognizing contamination.

Market milk and market cream are not so acceptable to the consumer when the minimum requirements of pasteurization are exceeded; consequently there is a delicate balance between pasteurization that guarantees the safety of the milk and that which is detrimental to the flavor or physical quality of the product. It appears that the phosphatase test will solve this important problem. This test is based on the property of the heat-sensitive enzyme phosphatase in milk to liberate phenol from phosphoric phenyl esters. When milk is heated, this enzyme becomes inactivated. During pasteurization at 143° F. for 30 minutes, 96% of the enzyme is destroyed. It is completely inactivated at 145° F. for 30 minutes. By quantitative determination, inadequate pasteurization or subsequent contamination with raw milk is indicated. The test has been modified considerably since it was first introduced, each development bringing to light its value and application.

Milk drinks, ice cream, and frozen desserts are made from combinations of pasteurized cream, milk, and concentrated milk products to which a variety of other ingredients are added. Bacterial contamination may occur from such added ingredients or from the growth of unfavorable bacteria during processing which may lower the quality of the final product. Modifications in microbiological methods require consideration as to adaptability to the product under examination.

It appears that yeast and mold count, predominating bacterial flora, presence of thermophilic, thermoduric, and coliform organisms are important in measuring quality. Products involved are various concentrated, condensed, and dried milk products, flavoring, sweetening, and stabilizing agents, eggs and egg products, fresh and canned fruits, nuts, etc. In this field there is a real need for better and more rapid methods that will be helpful in further maintaining quality.

GROWTH OF THE DAIRY INDUSTRY

The dairy industry has experienced phenomenal growth. A variety of factors have made contributions without which such growth would have been impossible. The cream separator, mechanical refrigeration, Babcock tester, milking machines, pasteurizers, mechanical can and bottle washers, combined butter churn and worker, highly efficient condensing and drying equipment, and modern machinery have made it possible to increase greatly the capacity of plants for efficiently handling milk and milk products and to improve in a considerable degree the quality of products reaching the consumer. Valuable contributions have been and are still being made by the sciences of bacteriology, chemistry, animal husbandry, and nutrition. Its rapid growth in so many varied fields could never have been accomplished had not the industry as a whole been appreciative of the value of quality control and receptive to the introduction of necessary methods of control and laboratory examination.

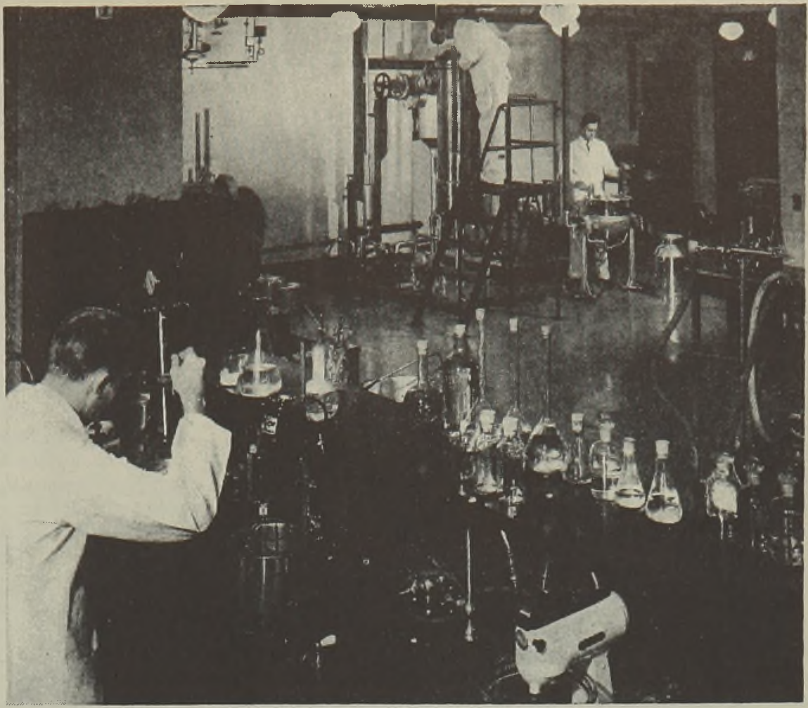
The cow has also made her contribution. In 1850 the average milk yield per cow was 1436 pounds; in 1924, 4167; and in 1942, 4739. In 1943, 26,670,000 cows gave a total milk production of 118,235,000,000 pounds.

Table I indicates the increased production of the more important dairy products over the past fifty years. Earlier figures are

TABLE I. PRODUCTION OF DAIRY PRODUCTS OVER HALF A CENTURY

	YEAR	1000 LB.	YEAR	1000 LB.
Butter	1850	300,000	1933	2,349,033
Cheese	1860	100,000	1942	1,109,336
Evapd. sweetened condensed milks	Began in 1850	....	1942	3,782,219
Ice cream and sherbet	Increase in production began 1900	....	1942	471,080 (gallons)
Malted milk	Began 1889	....	1943	49,000
Whole milk powder	Began 1909	....	1943	137,229
Nonfat dry milk solids	1919	50,000	1940	626,000

from census records; later ones from the statistical records of the United States Department of Agriculture.



Section of Research Laboratory with Milk Dryer in Background

COMPOSITION AND CONSUMER ACCEPTANCE

The federal definitions and standards of identity relating to composition and quality, and similar standards and definitions promulgated by state and local ordinances, make it necessary to keep a watchful eye over this phase of quality control. In 1884 the Association of Official Agricultural Chemists was organized in response to an acute need for standardizing the physical and chemical methods of analysis used in regulation and research in the food industry. Today these methods of analysis represent the accumulated effort of collaborative study over sixty years. In questions involving legality, only these official methods are recognized. In their development the motive has been solely that of accuracy. They frequently involve highly technical procedures and are usually time consuming. For these reasons they are not readily adapted to direct application in routine quality control in the dairy industry. They form the central pivot around which more practical methods of examination are built. Considerable progress has been made in developing such practical methods, but they are in further need of improvement. Rapid and accurate methods of analysis that will permit the continuous examination of samples during processing are necessary. Electrical methods of measurement involving colorimetry show promise in that direction. Microbiological methods discussed previously are customarily used in the examination of all manufactured dairy products.

Butter. Bacterial counts are of little value in judging butter quality. Most of the butter manufactured in this country is made from cream produced by a number of individual farmers. "Off-flavors" in butter are due largely to the action of microorganisms on cream used in the manufacture. During the past decade the butter industry, in cooperation with the Food and Drug Administration, has given a great deal of attention to the subject of sanitation and its relation to butter quality control. Vandeveer and Wildman's mold count method for evaluating decomposition in butter has furnished a means whereby the use of unsatisfactory cream may be detected. The Research Committee of the American Butter Institute has, in cooperation with other interested parties, led the way to the development of methods of determining mold and sediment in cream which can be used as a basis for judging the quality of this product. As a result the butter industry has made considerable progress in eliminating unsatisfactory sources of supply.

The physical and sanitary cleanliness of equipment and the control of contamination after manufacture is important. Potato dextrose agar is used in determining yeast and mold count. Modifications of the Burri smear culture technique is of considerable value. The pH value of butter serum is considered a measure of the active acid in the serum. Acidity represented by pH values between 6.4 and 6.8 tends to prevent spoilage during storage. The phosphatase test gives promise of being valuable in indicating the degrees of pasteurization received by the cream used in butter manufacture. A satisfactory method of judging butter quality involves scoring butter before and after incubation. Consumer packaged butter is incubated at 70° F. with 85–100% relative humidity for 8 days. Failure to drop one point is considered sufficient to justify the opinion that it will keep well in trade channels for a period of 6 weeks. Whether the quality in butter is evaluated on the basis of aroma, flavor, body, texture, color, or wholesomeness, the consumer places emphasis on uniformity of flavor and keeping quality. The art of making butter is fast becoming a science. Technical methods are being applied to every phase of the manufacturing operations with the result that more butter of excellent keeping quality is being produced.

Ice Cream. The consumer recognizes certain physical differences in the texture of ice cream as coarse, icy, snowy, flaky, sandy, and buttery, as well as certain flavor variations resulting from the nature and amount of ingredients used. To produce sufficient ice cream for the consuming public, the federal definition will probably provide for the use of all types of milk products. Furthermore, the public demands the addition of a wide variation of other ingredients. Quality control of ice cream therefore involves examination of the various ingredients used. Methods of examination will depend upon those that are best adapted to the product under observation. Progressive work is going on in many of the laboratories associated with this industry. Examinations are made of raw materials used. The finished products are subjected to chemical and microbiological examinations during and upon the completion of manufacture. Methods available at present require further study, and there is need of more accurate and improved procedures.

Cheese. The art of manufacturing cheese has come down through the ages. In the original methods there was much in the way of sanitation to be desired. In recent years the employment of men with college training in dairy manufacturing has had a beneficial influence on the industry. Methods involving sanitation have been improved. The cheese industry recognizes that good-quality cheese cannot be made from poor-quality raw materials. Combined effort on the part of the industry will accomplish the desired results, and progress is being made in this direction. The industry needs the tools of science to indicate the way. The Research Committee of the National Cheese Institute is collaborating with several of the leading state universities, with the Bureau of Dairy Industry in Washington, and with the Food and Drug Administration with the objective of developing more technical information relating to cheese manufacture. This program includes methods of cheese analysis, determination of extraneous matter, relation of raw milk quality to cheese manufacture, effect of pasteurization on cheese quality, and chemistry and bacteriology of cheese ripening. Steps are being taken to educate cheese milk producers further as to what constitutes satisfactory sanitation. These accomplishments point toward continued improvement of quality in this industry.

From the consumer angle, uniformity of body and flavor are most important. Science has given little help in this direction up to the present time. In cheese fermentations we are still compelled to let nature take its course; a broad field of opportunity awaits the future accomplishments of the research chemist in this field.

Soft products such as cream cheese, creamed cottage cheese, cottage cheese, Liederkranz, Camembert, and similar products require a milk supply of high quality if they are to possess the delicately fine flavor and aroma required. Microbiological methods are valuable in determining quality. The quality of the raw milk and failure to hold these products in storage at low temperatures may be responsible for the development of off-flavors.

EVAPORATED MILK. The Federal Standard of Identity for Evaporated Milk limits the fat and moisture content, and permits the addition of certain stabilizing agents and fortification with vitamin D by irradiation or addition of vitamin D concentrate. Butter fat tends to separate and form a cream layer at the top of the can, and salts, principally in the form of calcium citrate, tend to precipitate when evaporated milk is held at a warm temperature on continued storage. The food value of the product is not materially affected, but consumers take objection on account of the change in physical appearance of the product. The viscosity of evaporated milk has a direct bearing on its ability to hold the butterfat in suspension and prevent its separation. On account of the seasonal variation in the composition of milk, the definition of evaporated milk permits the addition of a stabilizer not in excess of 0.10%. The reason for such addition is solely to maintain the necessary chemical equilibrium between the mineral salts and casein. It permits adequate sterilization without coagulation of the casein. Although evaporated milk is a sterile product, individual cans occasionally become contaminated. This is usually the result of damage due to rough handling in transit, in which minute cracks develop in the seams of the can where bacteria gain entrance. Such contamination is readily recognized. The cans are swollen, and the milk is coagulated.

Bacteriological Plating Laboratory for Market milk

SWEETENED CONDENSED MILK. Federal definition limits this product with respect to fat and total milk solids. The bacterial count is usually less than 1000 per gram. The growth of certain bacteria is not necessarily inhibited by the presence of cane sugar even at a concentration of 42 to 45%. When held at warm temperatures for a considerable time, the bacterial count may increase. Within reasonable limitations this increase does not appear to be detrimental to the product. Yeast in sweetened condensed milk constitutes a contamination; resultant fermentation tends to make the product unmarketable. Molds are objectionable because they tend to form "buttons", so-called by the industry because of their appearance in the form of brown spots. Thickening of sweetened condensed milk frequently occurs on continued storage, especially at warm temperatures. This may be the result of bacterial fermentation or of chemical action. This chemical action is believed by some to be a result of interaction between the proteins and sugars. Lactose is present in a state of supersaturation. Should excessive separation of lactose crystals occur, they may settle at the bottom of the can and form what is termed "sugar separation". Quality control in this product consists of microbiological and physical examination before and after incubation.

NONFAT DRY MILK SOLIDS. Defatted or nonfat dry milk solids is the name recently given by Act of Congress to what was formerally known as dry skim milk. By federal definition it must contain not more than 5% of moisture. In 1929 the American Dry Milk Institute, representing the majority of nonfat dry milk solids manufacturers, established standards for this product. This action was stimulated by a growing need for some means to protect the consumer from inferior grades on the competitive market. These standards have been of inestimable value in bringing about a general improvement in the quality of this product throughout the United States in the short span of fifteen years. These standards define the general and specific requirements for extra grade and standard grade nonfat dry milk solids. They require compliance with federal and state regulations. Limitations regarding physical characteristics and limits for each grade are given with respect to butterfat, moisture, titratable acidity, sediment, bacterial account, and solubility. The grading pamphlet of the Institute includes the methods of analysis to be used.

Titratable acidity, bacterial count, and solubility index are expressed on the reconstituted basis. These figures enable the producer to make a ready comparison with corresponding figures of fluid milk with which he is familiar. In routine plant control, moisture is determined by the toluene distillation method. For practical purposes this method compares favorably with the official methods. It is reasonably rapid and can be applied during the drying operation. Solubility index is an empirical procedure and serves to measure the approximate insolubility of the product. In vacuum-drum-roller and spray-process nonfat dry milk solids this is important. It indicates any denaturing of the proteins through overheating during condensing or drying operations. Sediment tests are made by obtaining sediment disks from reconstituted material and comparing with standard photographic sediment disks.

DRY WHOLE MILK. A high-quality raw milk supply is necessary in the production of good-quality whole milk powder. The presence of butterfat at 26% makes it particularly sensitive to those factors which affect milk quality as related to butterfat. The use of copper, copper alloys, and iron in plant equipment is detrimental to the quality of whole milk powder in that it favors the rapid development of tallowiness and rancidity, and thereby makes the product unacceptable for human consumption. Such equipment has been replaced with stainless steel and glass-lined materials. Recent army specifications have required that whole milk powder shall not contain more than 1.50 p.p.m. of copper and not more than 10.0 p.p.m. of iron. A good grade of spray-process whole milk powder should meet the following specifications: moisture not more than 2.50%, fat not less than 26%, acidity not more than 0.15%, bacterial count not more than 6000 per cc. (equivalent to 50,000 per gram), sediment disk not in excess of No. 3, solubility index not more than 0.50 cc. Bacterial count, acidity, and solubility index are customarily determined on a reconstituted basis using 13 grams of powder in 100 cc. of water. This has the advantage of direct comparison with milk from which it is made. Laboratory methods are similar to those outlined by the American Dry Milk Institute for nonfat dry milk solids.

The packaging of whole milk powder is an important factor in quality control. The prevention of moisture absorption and changes in butterfat is necessary if the product is to keep beyond 3 to 6 months. The use of antioxidants in whole milk powder has met with limited success. For satisfactory storage this product is customarily packed under nitrogen or carbon dioxide gas in which the oxygen content is reduced to an absolute minimum. With satisfactory gas packing, whole milk powder will keep from one to two years.

STANDARDIZATION

Only when reasonably accurate methods of analysis were developed did standardization in the dairy industry become possible. Standardization involves making those necessary adjustments in raw materials whereby the product manufactured will adequately meet the requirements of a given standard of identity, a given legal definition, or a specific declaration on the label. Under the new Food, Drug and Cosmetic Act provision is made for the establishment of standards of identity. There is a definite tendency on the part of many states to adopt similar standards, which indicates a continued trend toward further standardization in dairy products. Progress in this direction will be delayed only by the lack of accurate and dependable methods of analysis. On account of the perishability of raw materials, standardization must be carried out rapidly. Continuous processing makes for economy and improved quality, but requires methods of quality control that can be applied during the operation. Such methods must have a reasonable degree of accuracy, as results have a direct bearing on operating efficiency. As standards of identity are increased or more rigid standards developed, a greater demand will be made for standardizing efficiency which will require new, rapid, accurate, and practical methods of laboratory control.

FORTIFICATION

Although milk is a highly variable product with respect to composition, there is a consumer tendency to expect milk and milk products to be of constant composition. The minerals and vitamins in milk vary with the type of feed and environmental conditions. The vitamins are detrimentally affected by exposure to heat, light, and air. In the interest of improved nutrition there is a growing tendency to restore to milk and milk products those lost values which result from production and manufacture conditions beyond our control. The science of nutrition is continuing to bring to light the dietary necessities of mankind considered individually and collectively. The relation of vitamin D to calcium and phosphorus and of vitamin B_1 to carbohydrate metabolism have been established. Current research is indicating similar relations between the vitamins and food intake. One school of thought concludes that, where restoration is highly desirable, fortification beyond the limits of restoration will better serve the nutritional welfare of the Nation. Whether it be restoration or fortification, quality and quality control considerations become highly important.

The official methods of vitamin assay are biochemical. They are time consuming. This has led to the development of a number of physicochemical methods which are reasonably satisfactory for routine quality control. These are being applied to the determinations of vitamins A, B_1, B_2, C, and niacin. Vitamin D is always determined by animal assay. When these methods are further perfected, it would be advantageous to the industry and regulatory agencies to make them official. Until such time, quality control will require a satisfactory interpretation of physicochemical measurements in terms of official procedure. With restoration and fortification goes the responsibility of maintaining those intrinsic values in food products until they are used by the consumer. Quality control must extend its supervision to considerations of correct packaging, transit, and storage; it must be kept in mind that the consumer accepts such foods solely in the interest of improved health through nutrition.

NUTRITION

The first essentials of nutrition require that food be safe and clean and possess the maximum of original nutritional values. Over the years regulatory officials have contended that many food products are served to the consuming public in a state of incipient decomposition. Until recently such statements could be substantiated only by visible evidence of decomposition, off-odors and -flavors, or special chemical and animal tests. More recently progress has been made in methods of chemical examination which conclusively establish the degree of decomposition. Unfortunately, like most original and dependable analytical methods they are complicated and time consuming. It appears that quality control in this field will simplify the complexity of present methods and lead to a further utilization of more rapid microanalytical methods.

During the past quarter of a century leaders in the field of nutrition have taught that there are important differences between the merely adequate and optimal in nutrition. Health means not merely freedom from disease but rather a positive quality of life and an ability to resist disease. To nutritional research goes the credit for the advancement of this ideal. In the interest of the public health, nutrition has become as essential as sanitation. Our newer knowledge of nutrition is fast becoming a source of information by which each individual may constructively develop his own life history involving positive health and longevity. These considerations directly affect our agricultural and industrial programs and the efficiency of the nation as a whole. In this field of human nutrition, quality control is destined to accept further responsibilities. Methods of analysis will be necessary whereby nutritional values may be measured in terms of ultimate satisfactory nutritional utilization of such foods by the consumer.

CONCLUSION

Some readers may feel that I have given too much credit to the dairy industry for what has been accomplished during the past fifty years. Though their local activities and interests may have indicated many undesirable conditions and unsatisfactory practices, I contend that such is not true of the dairy industry as a whole. There is no food product that requires so high a degree of quality control as do milk and milk products. Progressive application through the years has led to such marked improvement that the dairy industry today stands as an outstanding example of accomplishment in this field. To this program its leaders have given their fullest cooperation. This industry is indebted to thousands of scientists throughout the nation who collectively have made this possible. A sound foundation in the field of quality and quality control has been established on which the dairy industry may continue to build with credit to itself and service to the Nation.

The volatile constituents of food flavors, highly important to the acceptability of the foods, are treated in this paper as organic chemicals with conventional chemical and physical properties. Attention is given to the various characteristics of the volatile ingredients, and to the environment of the food, which influence volatilization. Among these characteristics, for each volatile substance, are vapor pressure at the temperature of evaporation, chemical properties, distribution in the food, and the pH and chemical nature of the whole. Evaporation of the volatile aroma coincident with that of moisture from the food is considered to be the most important cause for its volatilization. A table, based on vapor pressures, shows the respective spontaneous volatilities at room temperature of some 240 substances of interest to workers with foods. Suggestions are made for the use of this table for better control over volatilization of food flavor ingredients and specifically for flavor formulation and fixation.

VOLATILITY IN FOOD FLAVOR

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VOLATILITY is worthy of study by the food technologist as an important physicochemical characteristic of flavor. Volatile components are essential to the character and acceptability of many food flavors. These components are ordinary organic chemicals in most respects, distinctive only in so far as they stimulate appropriately the receptors of the sense of smell and, occasionally, those of taste.

Volatile flavoring ingredients may be present in concentrated condition, as are the sizable droplets of oil in skin cells of such fruits as oranges and lemons, in minute quantities beneath the skin of apples or strawberries, or distributed throughout the pulp, as in bananas. The volatile substances in cooked foods tend to be uniformly distributed but may also exist in concentrated particles, particularly when spices are used. Frequently, the volatile flavoring substances are either dissolved or are dispersed in watery fluids so that they tend to vaporize whenever any water evaporates from the food substance. No matter how they are distributed, there may be tight or loose chemical combinations that allow the volatile substance to be slowly released, as through the hydrolysis from enzyme action or as a result of volatile substances appearing on oxidation, putrefaction, or other slow chemical change.

Flavoring substances are of various chemical types; hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, lactones, anhydrides, esters, phenols, amines, sulfides, and mercaptans; saturated and unsaturated; aliphatic and aromatic. Some flavors are chemically stable whereas others have but short life, being susceptible to rapid loss on condensation or oxidation. These latter substances would not be important except that they are continuously produced in some foods by life processes or by decomposition in quantities sufficient to present useful odor.

The quantity of volatile flavor present in foodstuffs may be as great as one per cent as in citrus fruits, an amount too large to be consumed directly with the fruit. High flavor intensity is even more exaggerated in such concentrated sources of flavor as caraway seeds or cinnamon bark. In general, however, volatile flavoring is present in foods only in concentrations of thousandths or even hundred thousandths of a per cent.

CONSERVATION OF FLAVOR

Precautions that prevent loss of moisture from the food, such as use of high humidity, low air movement, moisture-tight wrappings, the frozen state, and uniform low temperature, generally conserve flavor as well as moisture. When flavoring substances are essentially insoluble in water, their evaporation with water is a "steam" distillation, even though it takes place at low temperature. Such steam distillation is effective for the gasification of even feebly volatile substances. Where there is true water solubility, however, the volatilization is distinctly less rapid for a given volatility and for the same quantity of water evaporated.

Flavoring substances dissolved in glyceride fats and oils may be present. Such substances evaporate from the oils slowly, either in the presence or absence of evaporating water. Solubility of aromas in fats is an example of physical "fixation"—that is, retardation of the evaporization of volatile materials when these are in the presence of less volatile substances with which they are miscible.

Fixation in the ordinary sense consists of the use of a small proportion of relatively high-boiling substance with an odor similar to, or at least harmonious with, the principal odor used. With such fixation there is a small amount of physical fixation in the sense of holding back evaporation of the more volatile ingredients, but a great deal more of character fixation, which is the holding steady of the desired odor type.

Since many foods have but slight physical fixation of the volatile flavors, loss of flavor may be rapid during the evaporation of water. Thus, on boiling in an open vessel the flavor may disappear rapidly. If the boiling is gentle, with careful retention of moisture, boiled foods will have maximum aroma. They may lose flavor later, however, if held warm or uncovered, or if evaporation takes place during cooling. There is unavoidable loss of much of the volatile flavor on even the most careful dehydration, this loss being dependent upon the quantity of water driven off rather than upon the temperature of the operation.

ACIDITY AND ALKALINITY

Changing the acidity or alkalinity is an important physicochemical means for reducing loss of flavor of some foods when water evaporates. For instance, the methylamines which contribute much to the odor of fish, especially shellfish, may be rendered nearly nonvolatile on lowering the pH by discreet additions of acid. People who do not like the amine odor may squeeze lemon juice on fish or may eat pickles with clam chowder, to reduce the amine odor intensity. On the other hand, those who like it may bring out the amine odor strongly with a pinch of sodium bicarbonate. Loss of acetic or other volatile acids from sour foods may be minimized during the boiling-off of water by raising the pH of the mix, where permissible, followed later by adding a controlled quantity of acid to release the volatile acids thus retained.

Combinations of sugars and volatile flavoring substances exist that protect volatile components against evaporative loss even when water evaporation takes place. An instance is the glucosidic compound of dextrose and methyl salicylate in the bark of black birch twigs and also in the leaves of wintergreen. Upon steeping, this nonvolatile glucoside breaks down completely by

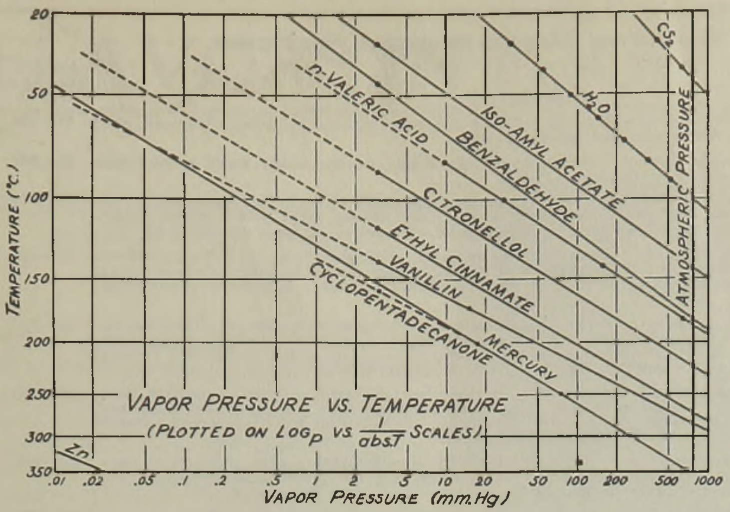


Figure 1

enzyme action, and the salicylate released may then be driven over on boiling the mass. Even a little of the methyl salicylate is set free on chewing the bark or the leaves containing the glucoside. Loose compounds that are practically nonvolatile when dry, but which break down on dissolving in water, have been discovered for a number of important flavoring agents. Their use for food purposes is described in a series of patents (*3*).

Flavoring ingredients range from simple substances of high volatility such as ethyl alcohol, acetaldehyde, acetic acid, ethyl acetate, diacetyl, and the methylamines, which boil below the boiling point of water, to substances with molecules of considerable size and complexity which may boil as high as 300° C. The tendency is for simple substances with small molecules to have odors of low specific intensity. A maximum of odor intensity usually is found in the middle ranges of molecular size, and the higher members of the various series again have weaker odors. There is a point in each chemical series where maximum odor exists for a given quantity of substance vaporized, with weaker odors for the same concentration of vapor possessed by members below or above that point. The more highly odoriferous members of most series have boiling points that fall in a comparatively narrow temperature range, 180° to 280° C.

BOILING POINT AND VAPOR PRESSURE

Boiling point alone is not a sufficient indicator for the volatility of a substance at any particular temperature, such as the 4° C. of a refrigerator or the 20° C. of room temperature, even when there is simple evaporation. A more nearly adequate indicator of the rate of spontaneous evaporation at any temperature is the vapor pressure at that temperature.

Chemical engineers have given much attention to the relation of vapor pressure to temperature and have devised convenient charting methods for finding values of vapor pressure at any particular temperature, over a wide range, when values are known at only a few points. Most of these methods are based on the integrated form of the Clausius-Clapeyron equation:

$$\log P = A - (B/T)$$

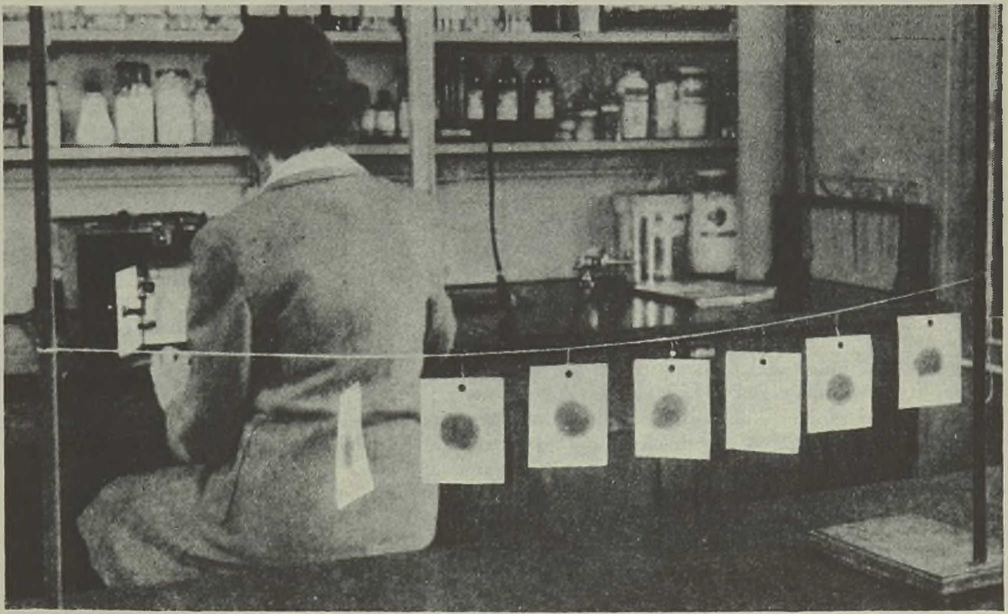
This equation may be interpreted as stating mathematically that a straight-line relation exists between the logarithm of the vapor pressure and the reciprocal of the absolute temperature. Calingaert and Davis (*1*) obtained empirical values for the constants of this equation as follows:

$$\log P = 7.991 - 1687/(T + 230)$$

where P = vapor pressure, mm. of mercury
T = temperature, ° C.

Figure 1 shows the vapor pressure of a number of flavoring materials plotted on a logarithmic scale against the temperature on a reciprocal scale.

Table I gives the vapor pressures at room temperature for some 240 typical important volatile substances, many of which appear in food flavors. These vapor pressures were computed in part from charts and nomographs and in part were determined experimentally. The table is an outgrowth and extension of one presented for perfumers' use nine years ago (*2*). Some fourteen classes of volatility are represented. Within each class, except



The volatility of an unknown flavoring material may be determined approximately by placing a drop on a sheet of bond paper hung in still air and noting the time required for the disappearance of the oily stain. By comparison with known materials, the volatility class of the unknown substance may be determined.

Table I. Classification by Volatility of Chemicals Involved in Food Flavors

Class	Vapor Pressure at 20° C. (68° F.), Mm.	Chemicals	Approx. Boiling Range
A	1.0–3.1	Aniline, benzonitrile, cineol, cymene, *o*-dichlorobenzene, *p*-dichlorobenzene, dichloroethyl ether, dipentene, ethyl heptoate, hexyl methyl ketone, *d*-limonene, phellandrene, phenol	174–196
B	0.56–1.0	Acetophenone, aldehyde C-8 (caprylic aldehyde), benzaldehyde, butyric acid, *p*-cresyl methyl ether, cyclohexanol, methyl benzoate, phenylacetic aldehyde, thujone	196–207
C	0.31–0.56	Benzyl acetate, citronellal, *m*-cresol, *p*-cresyl acetate, ethyl benzoate, guaiacol, hydroquinone dimethyl ether, isovaleric acid, menthone, methylchavicol, naphthalene, nitrobenzene, octyl acetate, octyl methyl ketone, phenylacetonitrile, propiophenone, salicyl aldehyde, styralyl acetate, *p*-tolyl aldehyde; estragon (tarragon) oil	207–217
D	0.18–0.31	Aldehyde C-9, bornyl acetate, bromostyrene, ethyl pelargonate (nonate), ethyl phenylacetate, isobornyl acetate, isopulegenyl acetate, linalyl acetate, *l*-menthyl acetate, methylacetophenone, methyl heptine carbonate, methyl salicylate, pulegone, *p*-tolyl acetate, *n*-valeric acid; lavender oil, pine needle oil, spike lavender oil, spruce needle oil, wintergreen oil	217–228
E	0.10–0.18	Alcohol C-8, benzyl alcohol, benzyl propionate, camphor, *n*-caproic acid, carvone, cuminic aldehyde, dimethylacetophenone, dimethyl benzyl carbinol, ethyl salicylate, fenchyl alcohol, isobutyl benzoate, linalool, menthol, *p*-nitrotoluene, nonyl methyl ketone, phenylacetaldehyde, dimethylacetal (Hyacyline), piperitone, safrole, terpenyl acetate, thymol; bois de rose oil, caraway oil, coriander oil, dill oil, peppermint oil, sassafras oil, spearmint oil	228–238
F	0.056–0.10	Alcohol C-9, aldehyde C-10 (*n*-decylic), anethole, borneol, caryophyllene, carvacrol, catechol monoethyl ether, citral, citronellyl acetate, cuminic alcohol, geranyl acetate, heliotropin (piperonal), *n*-heptylic acid, isoborneol, isobutyl phenylacetate, isopulegol, linalyl propionate, phenylethyl alcohol, phenylethyl propionate, phenylpropyl aldehyde, rhodinyl acetate; anise oil, star anise oil, thyme oil	238–248
G	0.031–0.056	Aldehyde C-11, anisaldehyde (aubepine), benzyl butyrate, citronellol, dimethyl anthranilate, diphenyl, eugenol, eugenyl methyl ether, geranyl propionate, α-ionone, isosafrole, linalyl butyrate, *p*-methoxyacetophenone, rhodinol, terpineol, terpenyl propionate; clove oil, copaiba oil	248–258
H	0.018–0.031	Alcohol C-10, aldehyde C-12 (methylnonylacetaldehyde), benzylidine acetone, *n*-caprylic acid, cedrene, cinnamic aldehyde, cinnamyl acetate, diphenylmethane, diphenyl ether, geraniol, β-ionone, hydroxycitronellal dimethylacetal (mugol), indole, isoamyl benzoate, isoeugenol, isoeugenyl methyl ether, methyl anisate, methyl anthranilate, methyl cinnamate, methylionone, perillyl alcohol, phenylacetic acid, phenylpropyl alcohol, terpenyl butyrate; cassia oil, cedarwood oil, geranium oil	258–269
I	0.010–0.018	Alcohol C-11, aldehyde C-12 (lauryl aldehyde), *n*-butyl salicylate, cadinene, ethyl anisate, ethyl cinnamate, geranyl butyrate, hydroxycitronellal, isoamyl salicylate, jasmone, β-naphthyl methyl ether (yara-yara), scatole	269–280
J	0.0056–0.010	Alcohol C-12 (lauryl alcohol), aceteugenol benzoic acid, anisic alcohol, *p*-chlorodiphenyl, cinnamyl alcohol, coumarin, cyclamal (Alpine Violet), dibenzyl, dibenzyl ether, myristic aldehyde, β-naphthol, β-naphthyl ethyl ether (nerolin), pseudo-aldehyde 16 (strawberry)	280–290
K	0.0031–0.0056	α-Amyl cinnamic aldehyde, apiole, dimethyl phthalate, ethyl citrate, ethyl myristate, *n*-hexyl salicylate, *o*-hydroxydiphenyl, naphthyl methyl ketone, pseudo-aldehyde 14 (peach), vanillin; celery seed oil, clary sage oil, parsley oil, patchouli oil	290–300
L	0.0018–0.0031	Benzophenone, cinnamic acid, diphenylamine, diethyl phthalate, ethyl sebacate, ethylvanillin (Bourbonal), geranyl tiglate, labdanum, 6-methylcoumarin, zingiberol	300–311
M	0.0010–0.0018	Benzyl benzoate, benzyl phenylacetate, benzyl salicylate, cedrol, *p*-cresyl phenylacetate, isobornyl salicylate, linalyl phenylacetate, phenyl phenylacetate, phenyl salicylate (salol), santalol, santalyl phenylacetate; costus oil, sandalwood oil, vetiver oil	311–321
N	Less than 0.0010	Astrotone, benzyl cinnamate, benzylisoeugenol, benzyl ketone, benzyl succinate, cyclopentadecanone, dibutyl phthalate, Exaltone, isoeugenyl phenylacetate, musk ambrette, musk ketone, musk xylene, β-naphthyl salicylate, phenylethyl phenylacetate, phenylethyl salicylate	Over 321

the first and last, *A* and *N*, are grouped substances with vapor pressures which differ no more widely than as 18 to 10. The average volatility relation from class to class is as 1.78 is to 1.00. Substances in group *F*, for example, four classes farther along in the table than those in class *B*, evaporate 1.78^{-4} or one tenth as fast, and those in class *J*, 1.78^{-8} or one hundredth as fast. Thus, in the convenient span of fourteen classes, a volatility range is encompassed that is 1.78^{14} or over three thousand fold in extent, yet with a volatility ratio from class to class of less than 2 to 1.

Approximate boiling points are given for some of the chemical classes, including esters, hydrocarbons, ethers, aldehydes, and ketones, which fall within the respective groups. Alcohols and acids are not so included. These compounds boil much lower for a given vapor pressure; stated differently, they have much higher vapor pressures than do the other compounds listed for the particular boiling point. Besides pure chemicals, such essential oils are included as evaporate principally within the limits of a single class.

SUGGESTIONS FOR USE OF TABLE

This table has proved useful in laboratory operations involving blendings, evaporation control, fixation, and the partial identification of organic materials. A mixture of two or more substances within a group will tend to evaporate more or less as a unit from the start of evaporation to the end. These blends will not change odor character noticeably during the evaporation. Where variation of odor character with time is desired, however, as in certain perfumes or flavors, a mixture can be made of, say, three to five such blends, each balanced esthetically, with several classes of separation between the successive blends. When such a mixture evaporates, the most volatile blend tends to evaporate first until it is essentially gone, then the next in order, and so on to the last. The odor at any instant will be principally that of the blend then evaporating most actively, influenced somewhat by the remaining ingredients and chiefly by those of the next following blends.

The table may be used for finding "character" fixatives, which will commonly be located in classes *K* to *N*.

Partial identification of volatile substances is often possible with the aid of this table if a small quantity of the unknown substance is available. A convenient technique is to place a drop of the unknown on a sheet of bond paper hung in still air, and observe the time which elapses before the transparent oily stain just disappears from the paper. If the sample is an old one, partially resinified, it should be freshly distilled before being tested. Substances of each of several classes of volatility which are evaporated at the same time, for comparison of speed of evaporation, aid in identifying the approximate class to which the unknown belongs. Having found the volatility class of the unknown, the ingredients in that class and the one on either side should be explored to find a satisfactory odor and evaporation match. At least the approximate boiling point can thus be obtained for further search, such as in using the boiling point values in the International Critical Tables.

Other applications of the volatility table will suggest themselves to food flavor research workers.

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FLAVORS IN FOOD FATS

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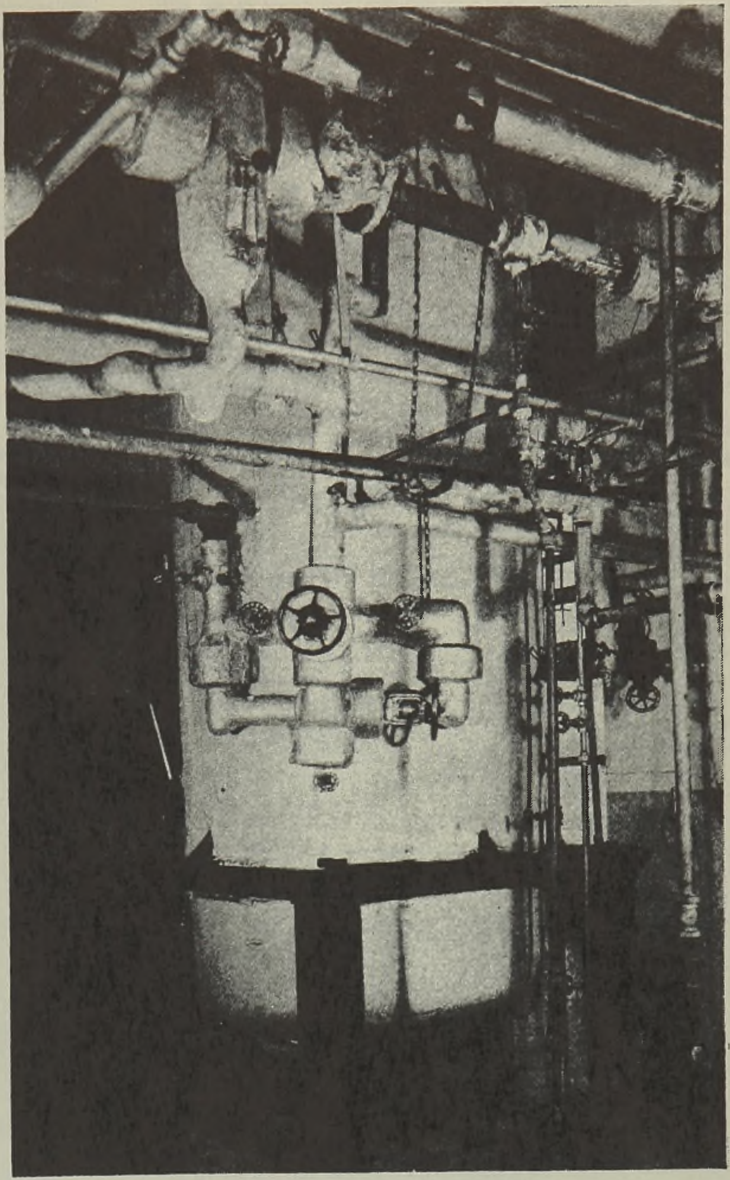

Pilot-Plant Deodorizer for Edible Fats and Oils

THE importance of food fats as a dietary staple is probably not popularly appreciated. In addition to furnishing a relatively large amount of the daily caloric requirements of most people, food fats are of major importance from a flavor standpoint. Some food fats are used to enhance the flavor of pastries, bread, and biscuits; others serve to add flavor to actual products in which they are found; still another group of food fats are carriers for other flavors in that they are themselves quite bland. Since one of the main principles of good nutrition is that food must be appetizing and appealing in taste, it is easy to recognize the contribution of food fats to eating pleasures.

Butter, margarine, olive oil, oleo oil, and open-kettle rendered, dry-rendered, and prime steam lard may be called the "flavorful" food fats.

Most prominent among the group of "invisible" food fats are those which are eaten as part of roasts, chops, steaks, etc. There is little doubt that they contribute flavor to the appetite appeal of these foods. Cream seems to add appreciably to the flavor of milk. At any rate, there is a marked difference in the flavor of skim milk and whole milk which is in favor of the latter. It seems probable that the fats which are naturally contained within cereals, fruits, and vegetables do not particularly influence the taste of those products.

Salad oils, shortenings, and bland lard comprise a group of fats which are, at least during normal holding periods, odorless and flavorless. Salad oils are processed from cottonseed oil, peanut oil, soybean oil, and corn oil. Shortenings are formulated from: (*a*) all hydrogenated meat fats or vegetable oils, (*b*) blends of meat fats and vegetable oils, and (*c*) blends of hydrogenated fats with unhardened fats or oils, either from vegetable or meat sources.

From the standpoint of domestic economy the most prominent vegetable oils are soybean, cottonseed, and peanut. Recently the production of soybean oil has slightly exceeded that of cottonseed oil which has always been a leader in the past. In times of normal world trade tremendous tonnages of palm, coconut, and other less well-known vegetable oils are imported into this country for processing into various types of food fats. The odorless and flavorless characteristics of the above-named group of fats are achieved only through the usual commercial practices of refining, bleaching, and deodorizing. In the raw state, with the exception of those products which were grouped with the flavorful fats, they all have characteristic and, to American palates, undesirable flavors and odors. These flavor and odor materials are apparently not part of the glyceride structure, but are due to foreign ingredients originating in the fruit, husks, or seeds from which each oil was expressed. All glycerides whose fatty acids consist of C_{12} or higher are considered to be free of flavor.

The characteristic and natural flavor of butter appears to be highly butyric in nature, blended with diacetyl, acetylmethylcarbinol, and various butyric, caproic, caprylic, and capric esters and other short chain fatty acids. The flavor of butter and margarine are also markedly influenced by the nature of the emulsion into which they are formed during processing. This factor can be readily demonstrated by a separation of butter fat and reemulsification in which the same flavors do not again prevail. The addition of salt to these products also exerts a marked effect; unsalted butter or margarine has a much less decided flavor.

Most margarines today are prepared from bland, deodorized vegetable oils. In some states formulation is based on deodorized combinations of vegetable oils, beef fats, and lard. In either instance the characteristic flavor of these products is furnished chiefly by pasteurized, cultured skim milk. The chief flavoring substances produced in these cultures are diacetyl and acetylmethylcarbinol. The organisms involved are *Streptococcus lactis*, *Streptococcus citrovorus*, and *Streptococcus paracitrovorus*. It seems probable that the chief difference between the flavor components of butter and margarine is the presence, due to hydrolysis in butter, of short-chain fatty acids and their esters.

RANCIDITY

While it is relatively easy to produce odorless and flavorless salad oils and shortenings, it is difficult to maintain this condition when the products are stored or held at elevated temperatures for long periods, ranging from a few weeks in some instances to several months in others. The principal changes involved come about through the processes of rancidity and reversion. The combination of oxygen with odorless and flavorless food fats tends to produce a number of degradation products which are characterized by undesirable flavors and odors. The predominant flavor, according to Powick (*8*), is due to heptylic aldehyde. Everyone who has had occasion to use food fats is well able to distinguish those flavors and odors which are termed "rancid".

There are several ways of avoiding or delaying the onset of the oxidative process on food fats. Recently the Meat Inspection Division of the Food Distribution Administration approved the use of nordihydroguaiaretic acid, lecithin, and tocopherols for shortening products containing meat fats. In 1940 the Bureau of Animal Industry, Meat Inspection Division, approved gum guaiac as the first edible antioxidant. While these antioxidants are valuable in varying degree in delaying the onset of rancidity in meat fat shortening or shortenings containing meat fats, they are of limited value with products made exclusively from vegetable oils. It seems probable that the field of edible antioxidants will be considerably extended during the next few years.

One of the chief advances made possible by the use of antioxidants has been the production of a bland lard which has a relatively high keeping quality. In years past, lard was not processed through the steps of refining, bleaching, and deodorizing because any one of these treatments lowers the keeping quality of the product to such an extent that it cannot be marketed successfully. The use of an antioxidant has now made possible the production of a bland lard which possesses the characteristic properties of other fully processed shortenings.

Flavor in meat fats as they are originally expressed or rendered in the raw state is quite different from that of vegetable oils in the raw state previously rated as undesirable. Many consumers believe that the unaltered flavor of lard is desirable for certain cooking and baking purposes. The same is true to a lesser degree of the beef fats, oleo oil, oleo stearin, and tallow. However, the introduction since World War I of hundreds of millions of pounds of the bland processed vegetable oils has apparently led the American housewife to demand this characteristic in any all-purpose shortening material. In the case of lard, as in one other which will be pointed out later, the question of the flavor of a fat and its stability to rancidity has been of tremendous economic importance to American agriculture. There is little doubt but that the demand for bland shortenings has had an effect upon consumer acceptance of the old style lards. The successful introduction of bland lard shortening holds great possibilities for regaining the popular demand for this fatty food and thus improving the agricultural economic position of this commodity.

REVERSION

Another effect of storage upon odors and flavors of food fats is typified by the phenomenon termed "reversion". At present the reversion of soybean oil has probably the greatest economic importance. Reversion is, in many instances, a misnomer since it tends to indicate that a fat which has been made bland will revert to the odor and flavor which it carried before processing. Actually the reverted flavor in soybean oil, lard, or tallow is not particularly characteristic of that fat in the undeodorized state. The reverted flavor of soybean oil is often termed "grassy" or "beany", progressing to "fishy". The reverted flavor of lard is not characteristic of the original taste and odor of this product when first rendered. The reversion of fish oil has some of the original characteristics of the undeodorized product but is still not the same flavor or odor. Tallow may be considered to revert to a flavor which is more nearly that of the original product in the raw state. Corn oil tends to revert after a time to a flavor which is undesirable and not characteristic of the original undeodorized product. Even cottonseed and peanut oils tend to revert to less desirable flavors after long periods. Fish oil has been prevented from becoming an important factor in the edible oil field because of its tendency to revert. Soybean oil has, over the past several years, averaged approximately one cent per pound lower in price than cottonseed oil. From chemical and physical characteristics other than the tendency to revert there would be no justification for such a price differential. Therefore, we have another instance in which the significance of a flavor factor in a food fat lowers the return to agriculture from a farm product.

There is little published material on the factors which are fundamentally concerned in reversion. Apparently the quantity of material which produces these reverted flavors and odors is in the range of only a few parts per million. Attempts so far, and there have been many, to isolate these flavor materials have been unsuccessful. It is known that hydrogenation of fats and oils is of some value in delaying reversion. It might also be mentioned in this connection that the reverted flavor of hydrogenated products is not the same as the reverted flavor of deodorized unhydrogenated fats and oils. Temperature as well as time is a factor in promoting reversion. It has not been clearly established whether the presence of oxygen is essential. Some experiments have tended to show that reversion takes place in the presence of very small amounts of oxygen, such as in the storage of hydrogenated soybean oil under nitrogen or other inert gases. However, in this instance it was probable that some traces of dissolved or occluded oxygen were present.

DIETARY EFFECTS OF RANCID FATS

The available literature concerning the deleterious effects of rancid fats in the diet is limited and inconclusive. There is little doubt that ingestion of rancid fats is detrimental to health, but whether the effect is direct or indirect has not been answered. The chief criticism of most of the research is that one cannot determine whether the ill effects resulted directly from a possible toxicity of the end products of rancidification or indirectly from the destruction by oxidation of various essential nutrients in the diet.

The direct toxicity effects have received little attention. Gyorgy *et al.* (*5*) observed some toxic effects which they ascribed to the oxidation products of linoleic acid. Some products of such oxidation may be absorbed in the intestines; for example, it has been shown that heptaldehyde is readily absorbed (*2*). If harmful products are absorbed, it must be to a minor extent; for it has been demonstrated that, when they are administered parenterally, they exhibit far greater toxicity than when taken orally (*3*).

Much more thought has been directed toward the indirect effects produced by the destruction of various essential factors. It has been suggested that, on the basis of their chemical structures, the following dietary essentials could conceivably be destroyed by oxidation: vitamins A, D, and E, carotene, pantothenic acid, pyridoxine, biotin, ascorbic acid, and the essential unsaturated fatty acids (*1*). Of these, only pantothenic acid and pyridoxine have not been studied from this point of view; all the others have been shown to be more or less completely destroyed in rancid fats.

The substance or substances in rancid fat that cause destruction are unknown. Steenbock's group found that vitamin A is not destroyed by oxidized glycerol, glyceric acid, glyceraldehyde, allyl alcohol, straight-chain aldehydes, methyl ketones with seven to twelve carbons, or decomposition products formed by the commercial hydrogenation of fats (*6*). The components which cause the destruction were not removed by steam distillation or by extraction with alcohol (*6*). Evans and Burr have concentrated the vitamin-E-destroying factor of rancid fats in the unsaponifiable portion (*4*). Sumner concluded that the intermediates of fatty acid peroxidation were the active agents but not the peroxides themselves (*9*). The loss of activity of vitamin A appears to be associated with the rapid formation of peroxides immediately following the induction period.

It has been suggested that destruction of linoleic acid and other essential fat acids may be an important factor. The feeding of oxidized fats has resulted in skin changes in rats (*10*) and in dogs (*11*) which were suggestive of linoleic acid deficiency, but in much more severe form. However, it has been shown that at the end of its induction period a fat still retains approximately 90% of its original linoleic acid, and some of the acid is still present when the peroxide value has gone as high as 500 (*7*).

In conclusion it must be said that the flavors or the absence of flavors in food fats are of paramount nutritional and economic importance. There is little doubt that fortune awaits the chemist or group of chemical research workers who are able to solve successfully the little known problem of reversion.

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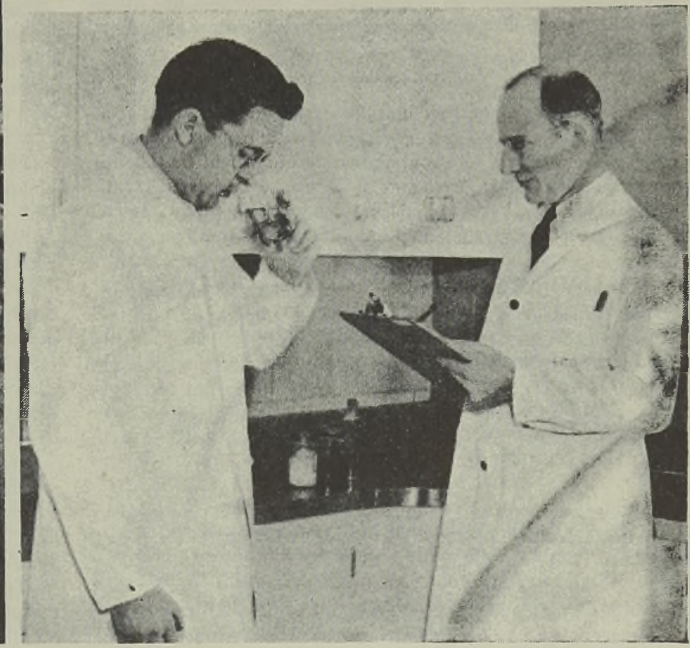

The Investigator at the Left is Working on the Determination of Keeping Quality (Rancidity) in Food Fats by the Active Oxygen Method. Below, Flavor Reversion in Soybean Oil Is Being Tested by the Only Satisfactory Test Now Known—Organoleptic.

The quality of meat includes many factors such as wholesomeness, appearance, composition, tenderness, flavor, juiciness, and nutritive value, most of which must be further subdivided. Development of adequate methods for measuring characteristics of meat has been and, in certain respects, continues to be a difficult problem. Breeding, age, sex, feeding, rate of growth, and other animal production factors have important effects on quality. Examples are presented, supplemented with a brief discussion of the significance of commercial meat grades. Of great influence on quality in meat are the following factors: processing, preservation, and preparation which involve methods of chilling, ripening, curing, smoking, freezing and freezer storage, dehydration, cooking, and other operations. Significant relations in this respect are discussed in some detail. Emphasis is placed on recent developments, particularly on those involved in the dehydration and freezing of meat.

QUALITY IN MEAT AND MEAT PRODUCTS

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THE opinion is widely held that meals should be built around meat. The high degree of palatability of this food, its ability to satisfy hunger, and important nutritive assets are largely responsible for this belief. The normal per capita consumption of meat in the United States is about 135 pounds per year, and it is among the foods regarded as relatively high priced. That interest in the quality of meat should be general, continuous, and intense is readily understandable.

Quality as applied to meat is a term too broad to have real significance. When it is broken down into its component parts, a number of factors are derived, such as wholesomeness, appearance, composition, tenderness, flavor, juiciness, and nutritive value, most of which must be further subdivided. Each of these characteristics is at least moderately well understood by the consuming public, and quality in any instance is determined by a conscious or subconscious consideration of all of them. Basically, however, differences in composition, tenderness, and other characteristics of meat may be due to any one or more of a number of causes.

WHOLESOMENESS

Although far from being unique in that respect, meat consumption could involve many dangers with respect to health. It is unnecessary to point out the risks that would be taken in eating meat from diseased animals or those harboring certain parasites, and meat that has been kept too long with the result that it has crossed the line between "fresh" and "spoiled". However, no large proportion of consumers in the United States is confronted with the necessity of taking such risks. Inspection services furnish protection to the bulk of our population. Notable among these services is the Meat Inspection Division of the War Food Administration, until February, 1943, a division of the Bureau of Animal Industry of the Department of Agriculture. It was established to administer the Meat Inspection Act passed by Congress on the same day in 1906 as the Food and Drug Act with which Harvey W. Wiley was so prominently identified.

There is, however, an unwholesome condition that may exist but is not detectable by present known practical methods of inspection. Reference is made to the possible infection of pork with trichinae (*Trichinella spiralis*). Unless destroyed in the processing or preparation of the meat, these parasites may cause the disease known as trichinosis. However, certain procedures in freezer storage and curing are now known to kill the organism. Cooking the pork to an internal temperature of 137° F. is likewise effective. Pork products which are usually eaten without cooking by the consumer are required at federally inspected establishments to be treated by one of these methods.

Except in farm and home curing and canning, spoilage of meat does not present a serious problem in the United States. This is due to a general understanding that meat is highly perishable and to the extensive use of good refrigeration facilities.

APPEARANCE

Although not necessarily a guide to quality in meat, appearance is always a psychological factor, and in some cases it is associated with characteristics of real importance to the consumer. Color is probably outstanding among those elements contributing to appearance. White fat, for example, is generally regarded as an asset in this respect and yellow fat a liability. Yet the latter, as often found in fresh beef, is caused in large measure by the deposition of carotene from the feed, carotene being the precursor of vitamin A. Therefore, yellow color of fat in beef may well indicate a higher vitamin A potency than white color and in that respect be an advantage, not a disadvantage.

The development of rancidity in fat is accompanied by a change to a yellowish color. Pork is especially predisposed to such changes. This color characteristic of fat that has acquired an objectionable flavor undoubtedly has much to do with the fact that meat consumers seek white fat.

There is considerable variation in the color of muscle or lean meat, especially in beef. The causes are not well established, except that it is rather clear that older cattle have darker-colored meat than younger cattle. However, it has not been shown that even dark-cutting beef, the extreme that meets with marked discrimination on the market, is necessarily low in palatability or other factors of quality important to consumers.

Another interesting example of change in appearance that may occur is that due to desiccation in low-temperature storage or freezer burn. Unless meat is well protected to prevent drying out, it loses moisture when stored at freezing temperatures, becomes pithy and spongy in appearance, and tends to lose the reddish color. There is little doubt that these changes are accompanied by undesirable changes in important factors of palatability.

COMPOSITION

Subsequent to the attainment of "chemical maturity", which comes early in life, there is little change in the composition of the muscle tissue of meat animals when considered on the fat-free basis. Nevertheless, the meat of cattle, hogs, and sheep, as they come to market, varies strikingly in both physical and chemical composition.

Breeding is one important basic cause of variation in composition. In one study (*12*), for example, the edible meat of steers of one type within a breed contained about 50% water, 35% fat, 14% protein, and 0.69% ash, whereas the meat of steers of another type within the same breed had about 56, 27, 16, and 0.74%, respectively. Even differences in composition of the meat from progeny of different sires within the same breed and type have been reported (*17*). There is actually prospect now of differentiation between such sires in terms of yield of the preferred cuts by their progeny (*16*).

As age and weight increase, meat animals in general tend to have more and more fat, with decreasing proportions of water, protein, and ash, under normal conditions of feeding. For example, it has been shown (*9*) that in hogs ranging from 50 to 325 pounds in empty body weight the fat content increased from about 20 to 55% whereas the water content decreased from approximately 60 to 35%, the protein from 16 to 10%, and the ash from about 3 to 2%. When animals of widely differing ages but of approximately equal fatness are fed under uniform conditions for the same period of time, the fat content of the meat tends to vary with age. Work at a number of research institutions, especially with cattle, has indicated this to be true.

The dressed carcasses of heifers contain higher proportions of fat and total edible meat, with lower proportions of lean meat and bone, than the carcasses of steers of the same breeding, age, and feeding. Wether lambs tend to be fatter, although slightly lighter in weight, than comparable ram lambs. Results of different studies on the comparative composition of barrows and gilts, however, are inconsistent.

Different feeds, feed combinations, and levels of feeding or daily allowances are rather generally known to have distinct effects on the composition of meat of the animals to which they are fed. Perhaps the outstanding example in this country is the relatively strong tendency of corn feeding to result in the deposition of fat.

In one notable study (*13*), four combinations of levels were compared in the feeding of pigs. They were as follows: high followed by high, high followed by low, low followed by high, and low followed by low. Each animal was slaughtered when it attained the weight of 200 pounds. The separable fat content of the carcasses was 38, 33, 44, and 27% for the high-high, high-low, low-high, and low-low groups, respectively. Corresponding percentages of lean tissue were 40, 45, 36, and 49, and of bone, 11, 11, 10, and 12.

The variation that occurs in the composition of the meat fat itself is influenced by the characteristics and proportion of the fat in the feed. This influence, exemplified by the fat of such feeds as soybeans and peanuts, is responsible for the production of most of the soft pork in this country.

The war created an urgent need for meat, as well as other foods, in space and weight-saving form for long-distance shipment. Dehydration was the answer, but much research was required and has been conducted during the emergency on this method of food preservation. The chemical composition of dehydrated meat is influenced by the composition of the raw material, the extent of the removal of moisture, and any losses or removal of other constituents, such as fat, that occur during processing. A typical analysis for fresh, closely trimmed pork ready for drying is moisture 65.3, ash 0.9, protein 18.8, and fat 15.0%. Dehydrated to 10% moisture content, but with no fat or other loss in the processing, meat of this composition should yield a finished product containing approximately 2.3% ash, 48.7% protein, and 39% fat. This would be in line with WFA specifications for this product, which provide in part that it shall not exceed 10% in moisture and 40% in fat.

GRADES

The numerous factors that affect quality and the extremely wide variation in the quality of meats and meat products as they are offered on United States markets make it essential that the grading system be the best possible for recognizing differences. Beginning with beef in 1927, the United States Department of Agriculture made available a meat grading and stamping service. The undertaking was expanded to include lamb and mutton in 1930 and veal in 1931. In December, 1942, the federal grading and stamping of meat became mandatory in connection with the application of price ceiling regulations. All meats, except pork, expected to go into commercial channels were soon covered by this program.

Considerable Department of Agriculture research has been directed toward the characterization of meat grades in definite, measurable terms. Noteworthy progress has been made, particularly in establishing the composition of the different grades. Highly useful values are now available, for example, not only for the mean composition of dressed lamb carcasses of any of the six recognized grades—prime, choice, good, commercial, utility and cull—but also for the primary cuts from such carcasses.

TENDERNESS

Excepting unwholesomeness, there is no attribute of meat more of a liability than toughness. There is insufficient knowledge on which to base a fully satisfactory statement as to the basic factors responsible for toughness. However, the following inherent factors, at least, are now considered by many to have a bearing on toughness or tenderness: diameter of muscle fibers and of muscle-fiber bundles that give the grainy appearance to meat, proportion and distribution of connective tissue, fatness in the gross and, especially, the proportion and distribution of fat within the muscle.

Several objective methods for the determination of tenderness have been developed. The method in successful use by the Department of Agriculture and a number of other research institutions was described in its original form in a Department publication (*3*) and later improved cooperatively by the Bureau of Animal Industry and the Kansas Agricultural Experiment Station. Values obtained with the apparatus represent resistance of cooked meat to shearing action.

The tenderness of meat is influenced by many factors. Breeding of the animal may logically be mentioned first. As an example of this influence, it was found in a study of first-generation lambs of Lincoln × Rambouillet, Corriedale × Rambouillet, Columbia × Rambouillet, and Romney × Rambouillet breeding that the meat of the Lincoln-sired animals was clearly the least tender. Among the second-generation crossbred lambs, those of Romney × Rambouillet breeding ranked lowest in this respect (*6*).

Generally speaking, significant differences in tenderness of meat have not been produced experimentally by different feeds or rations, when the feeding was such as to result in about the same rate of gain and the same degree of fatness in the animals. Yet feeding can be responsible for significant differences. A good illustration is found in the case of paired lambs, given a certain feed combination by the Department so that one animal of each pair made a normal gain whereas the other made no appreciable gain in weight. The cooked meat of the normal gaining lambs was approximately 25% the more tender (*1*).

It is not necessarily true that the meat of the young animal is tender and the meat of the old animal tough. However, there is a general tendency for tenderness to vary inversely with age. Research has indicated, surprisingly, that the meat of exercised cattle is more tender than that of cattle which have little opportunity to move around (*18*). One should bear in mind, incidentally, that there are variations in tenderness among the various cuts and muscles of the same animal.

Making use of enzymes that occur in the meat itself is a widely known method of tenderizing. This ripening may involve a period of some days or weeks. Temperatures of about 34° to 38° F. are commonly employed. In certain Department work the tenderness of porterhouse steaks held at 34° was approximately 28% greater at 35 days than at 5 days after slaughter of the cattle (*10*). Another method that makes use of enzymes occurring in the meat was developed several years ago and applied commercially in the United States. The process employs relatively high temperature with ultraviolet light for a short time. Only one report has come to the attention of the writer in which the extent of the tenderization was given exactly. Beef held at 60° F. and exposed to ultraviolet light 48 hours, then stored at 36° for an equal period, was about 10% more tender than beef held at 36° throughout a period of 96 hours (*7*).

To increase tenderness, certain enzymes have even been applied to meat and sausage casings. Tenderized ready-to-eat hams, which have become so popular in recent years, are smoked under such conditions that they are really cooked at the same time. The tenderizing that occurs in the processing is believed to be primarily due to the heat of the cooking, not to the curing or smoking.

One of the most significant findings of recent years in relation to tenderness of meat is the effect of freezing. It was shown (*8*), for example, that beef frozen at +20° F. was approximately 12% more tender than unfrozen beef. When the freezing temperature was −10° or −40° the effect was about 18%. In another study (*10*), beef ripened 5 days at 34° F. and then frozen at −10° was fully as tender as beef ripened 35 days.

Cooking undoubtedly is a major factor influencing tenderness. Research has shown, among other things, that when meat is suspected of lacking tenderness, the use of a low cooking temperature for a relatively long time is appropriate.

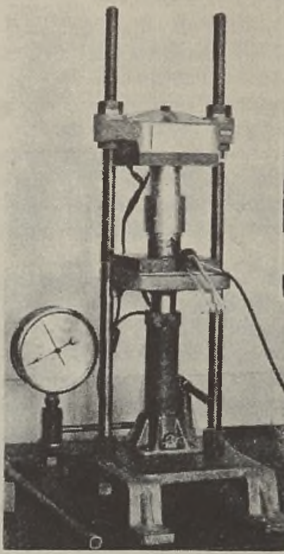
FLAVOR AND JUICINESS

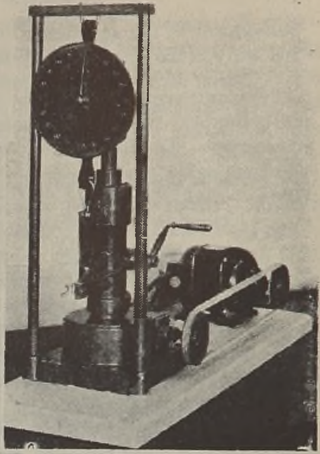
The components which together impart the characteristic fresh meat flavor are not accurately identified, although they are believed to consist of water-soluble extractives, lipides, small amounts of carbohydrates and salts, or compounds produced from these products and proteins by cooking, enzyme action, or both (*11*). Of course there are several modified meat flavors such as thoseof ripened fresh meat, cured meat in both the freshly processed and aged forms, and even rancidity associated with fat breakdown. Research workers are still largely dependent upon organoleptic methods for determination of differences in this characteristic of meat.

An example of difference in fresh meat flavor is found between beef from young animals and that from more mature cattle. The latter is usually more intense in flavor. Perhaps an even more striking difference is found between lamb and mutton. In a closely controlled study by the Department of Agriculture, the meat of full-fed lambs was not materially different from that of limited-fed lambs in the intensity of flavor of lean (*1*). However, the former was rated significantly higher in desirability of flavor.

In emergency research by the Department on methods for dehydration of meat, flavor of the product was a point of major importance. Pork, frozen, ground, and then dehydrated in moving air at 120° F., had a definitely better flavor rating in the freshly processed state than similar meat that was precooked and subsequently dried at higher temperatures in air or vacuum. The former product, however, presented a somewhat serious keeping quality problem (*5*).

Below. **Apparatus Used in Determining Juiciness (Expressible Juice Content)**





Above. **Apparatus Used by Bureau of Animal Industry for Determining Tenderness (Resistance to Shearing) of Meat**

In a particular instance the problem relating to juiciness may be stated as follows: How juicy is the meat and how rich is the juice? A serious obstacle to research on this characteristic of meat also has been the lack of adequate technique. However, with respect to the quantitative phase of the problem, this obstacle is now rather well overcome through the development of certain mechanical methods. The method offered by the Bureau of Animal Industry produced values which gave coefficients of correlation of approximately +0.90 with committee judgments (*15*). Elimination of the personal factor in evaluating juiciness of meat would seem to be justified. A satisfactory method for replacing subjective determinations of quality is yet to be devised.

Only limited research has been done to determine the factors responsible for variations in juiciness. As an example of results, a direct relation between fat content of beef and quantity of juice has been reported (*2*). On the other hand, the latter was found to decrease with increase in degree of doneness in roasting (*4*, *14*, *15*). Fatness of meat has also been reported to have a highly significant effect on richness of the juice (*2*), although it is probable that components other than the fat of the juice also have a bearing on this factor of palatability.

NUTRITIONAL PROPERTIES

Meat is generally regarded as a high-protein food. Therefore, questions may logically be asked as follows: How does the biological value of meat protein compare with that of other foods? Does it vary significantly among the different kinds of meat? What is the supplemental value to the proteins of cereals and cereal products? Present knowledge on these points is to the effect that the proteins of lean meat are superior to those of cereals and cereal products, at least equal to milk proteins, and possibly somewhat inferior to egg proteins. When the meats do not vary materially in connective tissue content, the proteins of lean beef, pork, veal, and mutton appear to have practically the same biological value. In proper combination with the proteins of cereals and cereal products, the use of meat proteins results in the biological value of the combination equaling that of the meat proteins themselves.

In research on dehydrated meats, it was observed (*5*) that the protein was most nutritious when the raw meat contained a minimum proportion of connective tissue and when the processing was carried out as rapidly and at as low a temperature as practicable. Moreover, for the most part, the digestive coefficients for the protein in the dehydrated product compared favorably with those previously reported for meat in general.

With respect to certain vitamins, meat and some meat products are now known to be good sources. In fact, vitamin A is abundantly supplied by liver. Of the B vitamins, riboflavin is found in extremely large amounts in liver, heart, and kidneys. Niacin also occurs in large amounts in these products, especially in liver and kidneys. Thiamine is supplied to an intermediate extent by these same three products, to only a slightly lesser extent by beef, lamb, and veal muscle, and very liberally by pork muscle.

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[*End of Symposium*]

Predicting Volume Increase of Perbunan Compounds in Petroleum Products

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A study has been made of the volume increase of Perbunan compounds immersed in various petroleum products. As a result of this work a method has been developed for calculating the volume swell of a Perbunan compound when it is immersed in a given petroleum product under certain test conditions. The work of prediction or calculation of volume increase has been simplified by the construction of two graphs which may be used with experimentally determined constants of swell and extraction.

IN THE formulation of oil-resisting synthetic rubber stocks, it is frequently desirable to know what will be the approximate volume increase of the proposed compound in a certain immersion medium under specific test conditions. If available volume increase data on a synthetic rubber compound could be used in formulating the new recipe, the amount of work required to establish the new stock could be considerably reduced. The purpose of this paper is to show the development of a relatively simple system to predict the volume increase of Perbunan compounds.

Catton and Fraser (*3*) reported that the swelling of neoprene compositions depends on the volume of neoprene in the compounds. A subsequent paper (*4*) showed how the volume increase of a compound may be calculated if the oil immersion medium is used as a softener in the compound.

Aniline point, viscosity-gravity constant, and Diesel index (*2*, *4*, *5*, *7*) may be used to measure the properties of petroleum products which govern the swelling characteristics of synthetic rubber compounds. Also, the swell of Perbunan compounds (*10*) is a function of the aromatic content of the gasoline. These factors will not be considered in this discussion; rather, specific values will be presented for a variety of petroleum products, and an attempt will be made to relate the effect of various compound changes on the resistance of Perbunan compounds to petroleum products.

If, as previously stated, the swelling of a synthetic rubber compound is due to swelling of the polymer,

$$V = KP/100 \tag{1}$$

where V = % volume increase of compound
K = % volume swell of cured polymer
P = % polymer by volume in compound

Volume increase results were obtained in duplicate by A.S.T.M. method D471-43T (*1*), except that a Jolly balance was used in weighing. Table I shows volume increase data for Perbunan compounds containing various amounts of carbon black. The polymer swell values for each gasoline were calculated, and the deviation from the average was found to be small.

Additional K values, or percentage volume swell of the polymer, are reported in Table II. Two concentrations of black were used, and the K values for the different polymer concentrations were found to be nearly equivalent. The data cited appear to demonstrate that the swell of Perbunan compounds in various immersion media is due to the swell of the polymer, the compounding ingredients serving to dilute the Perbunan and thus reduce the swell of the total compound.

This conclusion assumes that all the compounds have approximately the same state of cure and that there are no extractable softeners in the compound. In this work the same accelerator, sulfur concentration, and time of cure were used. The recipes are the type in which the state of cure should be similar, even though the amount of loading is widely varied.

Table I. Volume Increase of Perbunan Compounds in Two Gasolines, after 168 Hours at 25° C.

(Base recipe: Perbunan 100, zinc oxide 5, stearic acid 1, benzothiazyl disulfide 1, sulfur 1.5, semireinforcing furnace black as indicated; cured 60 minutes at 287° F.)

Parts Black by Wt.	% Perbunan by Vol.	% Vol. Increase in: Gasoline 1[a]	% Vol. Increase in: Gasoline 2[b]	% Vol. Swell of Cured Polymer (*K*) in: Gasoline 1[a]	% Vol. Swell of Cured Polymer (*K*) in: Gasoline 2[b]
50	77	59.0	24.5	76.6	31.8
75	70	52.3	22.8	74.8	32.6
100	63.8	47.6	20.7	74.5	32.5
150	54.5	40.3	17.5	74.2	32.1
175	50.8	37.7	16.4	74.2	32.3
			Average *K* value	74.9	32.3

[a] 60% 65-octane gasoline, 5% benzene, 20% toluene, 15% xylene (by volume).
[b] 100-octane aviation gasoline, lot A.

Table II. Polymer Swell of Perbunan in Petroleum Products

(Base recipe: Perbunan 100, zinc oxide 5, stearic acid 1, benzothiazyl disulfide 1, sulfur 1.5, semireinforcing furnace black as noted; cure 60 minutes at 287° F.)

Parts Black by Wt.	Fluid	Aniline Point, ° F.	Temp., ° C.	% Vol. Increase 70 hr.	% Vol. Increase 168 hr.	% Vol. Swell of Cured Polymer (*K*) 70 hr.	% Vol. Swell of Cured Polymer (*K*) 168 hr.
...	Gasoline 1	..	25	..	..	75.6[a]	74.9[a]
...	Gasoline 2	..	25	..	..	31.6[a]	32.3[a]
75	Petroleum base oil 3 (*1*)	158	100	22.0	22.6	31.4	32.3
150	Same	..	100	16.7	17.3	30.6	31.8
75	Extreme pressure lubricant	181	100	13.9	16.3	19.8	23.3
150	Same	..	100	10.0	12.1	18.4	22.2
75	WS 491 hydraulic oil	177	100	9.8	9.0	14.0	12.8
150	Same	..	100	7.3	7.2	13.5	13.2
75	Esso aviation oil 100	256	100	−0.8	..	−1.1	..

[a] Average for range of loadings (Table I gives composition of gasolines).

EFFECT OF EXTRACTABLE SOFTENER

The effect of extractable softener on the volume increase of an oil-resisting synthetic rubber stock was discussed by Juve and Garvey (*9*). They stated that, on immersion in hot oil, the volume increase is reduced by three factors: change due to heat hardening, hardening due to loss of softener, and evaporation plus extraction of softener. The volume increase of a compound containing no softener would be influenced only by the first factor. It has been further pointed out (*6, 11*) that the swelling characteristics of the immersion medium may be altered by the presence of plasticizer which may have been extracted from the synthetic rubber stock.

For compounds containing extractable softener, Equation 1 may be modified by a term which indicates the amount of softener extracted from the compound:

$$V = (KP/100) - ES \qquad (2)$$

where E = extract coefficient
S = % softener by volume in compound

Extract coefficient E is defined as per cent by volume of extractable softener divided by per cent by volume of softener in the compound. In most synthetic rubber compounds there is an extract which is due to stabilizer, fatty acid, emulsifier, etc. No attempt will be made to determine specifically the extract due to these factors, and for purposes of calculation all extract will be attributed to softener.

Table III illustrates how this method of calculation can be applied to compounds containing an extractable softener. The agreement between the calculated and experimental values is excellent. The extract coefficient for tributoxy ethyl phosphate appears to be about 0.8. This means 80% of the softener was extracted by the gasoline.

Volume increase data were obtained on seven stocks under six conditions of immersion in petroleum products. Six stocks contained softeners commonly used in Perbunan, and the seventh was without softener. Polymer swell value K was determined on the stock which contained no softener. Extract coefficient E was obtained by substituting the known values of K, P, S, and V in Equation 2 and solving for E. Volume increase data and extract coefficient values are included in Table IV.

The outstanding point in these data is that the extract coefficient for a given softener appears to be but little influenced by the immersion media. The extract coefficients in the two gasolines and in the three hot oils are quite similar.

SIMPLIFICATION OF CALCULATIONS

The calculations for determining volume increase are somewhat involved. This procedure has been considerably simplified by use of three plots; two are given in Figure 1 and the other in Figure 2. In the top half of Figure 1, parts carbon black by weight are plotted against per cent Perbunan by volume for compounds containing 0, 10, 20, 30, 40, and 50 parts softener having a specific gravity of 1.0. The bottom half is a plot of per cent volume increase plus per cent by volume of extractable softener against per cent Perbunan by volume for various K values (per cent swell due to cured polymer). From the two graphs of Figure 1 it is possible to determine $V + ES$ (volume increase plus volume of extractable softener). The per cent volume of extractable softener, ES, can be obtained from the extraction coefficient, specific gravity of softener, and the plot in Figure 2. This figure is a graph of parts carbon black by weight against per cent softener by volume, S, for compounds containing 10 to 50 parts of softener. The volume increase of the compound, V, is then easily determined by difference.

To illustrate how these graphs are used, let us calculate the volume increase of a Perbunan compound containing 75 parts of semireinforcing furnace black and 20 parts of tributoxy ethyl

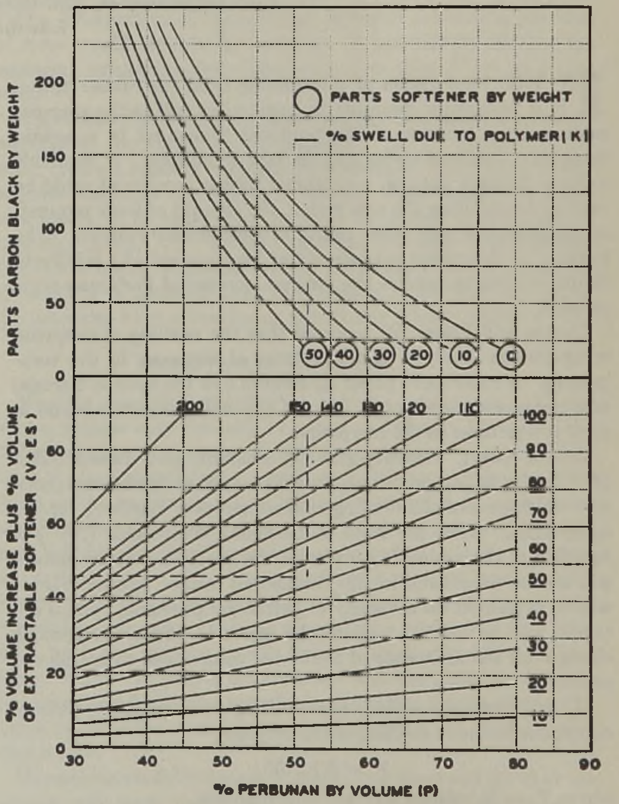

Figure 1. Calculation of Volume Increase of Perbunan Compounds

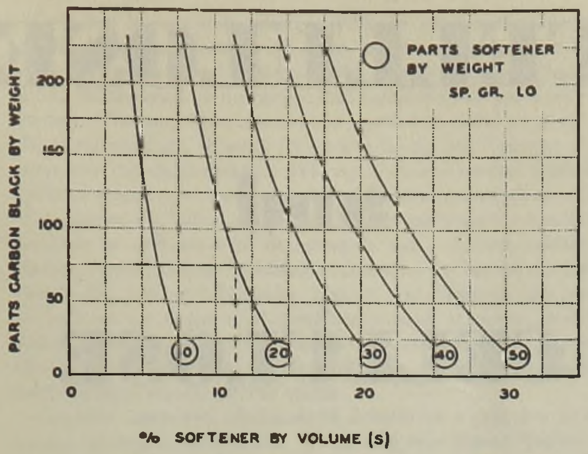

Figure 2. Calculation of Volume Increase of Perbunan Compounds

phosphate after 7 days in 40% aromatic gasoline. From previous data it is known that the K value or per cent swell of the polymer is 75 for a Perbunan compound in this gasoline.

The figures are constructed using parts black by weight and parts softener by weight. The softener has a specific gravity of 1.0. If the softener does not have a gravity of 1.0, it must be corrected to this basis. This may be accomplished by expressing the softener as parts by volume, since a specific gravity of 1.0 means that parts by volume are equivalent to parts by weight. Thus for 20 parts tributoxy ethyl phosphate (specific gravity 1.02), 20/1.02 = 19.6.

In Figure 1 the dotted line indicates how a value of 46% swell represents the volume increase of the compound plus the volume of extractable softener, $V + ES$. In Figure 2 the dotted line indicates how the per cent softener by volume, S, is determined. A line is extended from 75 parts black by weight to the value of 19.6 parts softener. This is then extended downward, and S is found to be 11.6%. The extract coefficient, K, for tributoxy ethyl phosphate is 0.8. Hence $ES = 11.6 \times 0.8 = 9.3\%$ volume of extractable softener S. Then $V = 46 - 9.3 = 36.7\%$ volume increase of the compound. The experimental value was found to be 37.2%.

Table III. Calculation of Volume Increase of Perbunan Compounds Containing Extractable Softener

(Base recipe: Perbunan 100, sine oxide 5, stearic acid, 1, benzothiazyl disulfide 1, sulfur 1.5, black and softener as indicated; cured 60 minutes at 287° F.)

Semireinforcing furnace black	75	150	75	150
Tributoxy ethyl phosphate	20	20	40	40
% Perbunan by volume	61.7	49.4	55.3	45.3
% softener by volume	11.5	9.3	20.7	17.0
% by vol. of extractable softener (ES), as measured by % shrinkage of dried volume-increase specimen[a]	9.1	8.3	16.2	13.8
$E = \dfrac{\%\text{ extractable softener by vol. }(ES)}{\%\text{ softener by vol. in compound}}$	0.79	0.90	0.79	0.81
$V = (KP/100) - ES;\ (K = 74.9)$	37.1	28.7	25.1	20.3
% vol. increase[a]	37.2	30.0	25.9	19.8
Difference between calcd. and exptl. volume increase	−0.1	−1.3	−0.8	+0.5

[a] After 168 hours at 25° C. in gasoline 1 (containing 40% added aromatics).

The Perbunan used in this study came from the same large blended lot of polymer. Tables III and IV indicate slight differences in the K values, on the same recipe and immersion fluid. In Table IV K was determined on a stock containing no softener. This stock was run in the same series as those containing the various softeners. The experience of this laboratory has been that the variation of several volume increase determinations in 40% aromatic gasoline run at different times by the same operator is 2%. When the volume increase becomes smaller, the percentage error tends to increase. When these data in Tables III and IV are examined in the light of the limitations of precision, the variations do not appear to be too great.

In normal practice other factors than actual measurement which will also affect results are variation from lot to lot of the swelling power of the various classes of petroleum products, the state of cure of the stock, and the small variation in composition between various mixes of compound. Commercial practice on most specifications takes these factors into consideration when volume increase limits are set, so that these factors and other possible limitations do not appear to detract from the usefulness of this method.

Gee reported (*8*) that the absolute swelling of rubber in a good swelling agent is reduced by reinforcing fillers. Preliminary evidence indicates this to be true for Perbunan, but the differences are small in the liquids with which Perbunan compounds come in contact in service. This point is the subject of another investigation.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of Mrs. M. F. Bergh in securing the experimental data.

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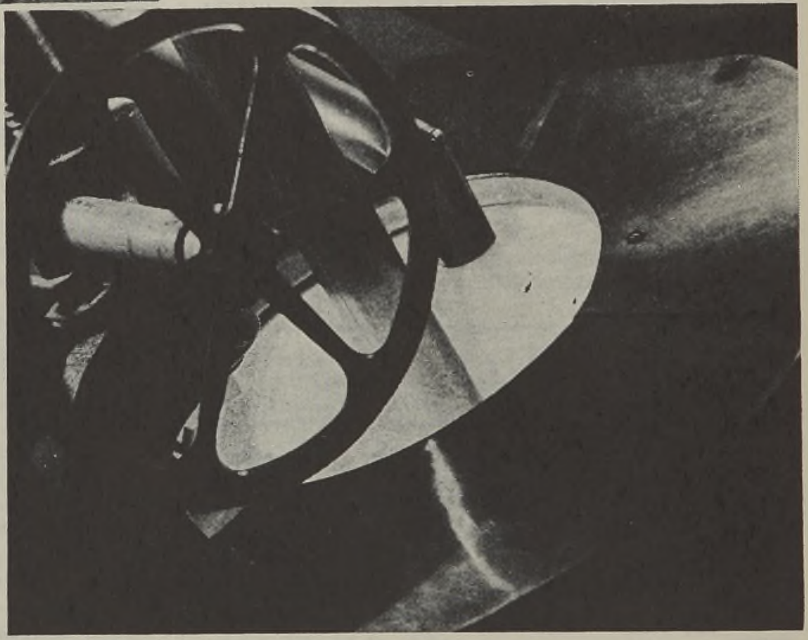
Table IV. Volume Increase and Extract Coefficient Values of Perbunan Compounds after Immersion in Petroleum Products

(Base recipe: Perbunan 100, zinc oxide 5, stearic acid 1, semireinforcing furnace black 75, benzothiazyl disulfide 1, sulfur 1.5, softener 20)

Immersion			% Volume Increase with:								Extract Coefficient E with:					
Hours	° C.	Fluid	No softener	Dibutyl phthalate	Dibutyl sebacate	Refined coal tar[a]	Coal-tar derivative[b]	Diphenyl phthalate	Tributoxy ethyl phosphate	Value of K with no softener	Dibutyl phthalate	Dibutyl sebacate	Refined coal tar[a]	Coal tar derivative[b]	Diphenyl phahalate	Tributoxy ethyl phosphate
168	25	Gasoline 1 (40% aromatics)	51.3	36.9	35.4	41.8	38.4	37.9	35.7	73.4	0.75	0.81	0.47	0.66	0.89	0.82
168	25	100-octane aviation gasoline[c]	19.3	7.4	6.6	13.0	10.4	8.9	8.8	27.6	0.84	0.84	0.44	0.65	0.90	0.71
70	100	Petroleum base oil 3	21.8	9.4	7.5	14.1	11.2	9.2	8.9	31.2	0.86	0.95	0.56	0.75	1.00	0.89
70	100	WS 491 hydraulic oil	9.7	−1.1	−2.3	2.3	0.7	−0.8	−3.1	13.9	0.85	0.87	0.65	0.73	1.00	1.00
168	70	WS 491 hydraulic oil	7.8	−3.5	−4.1	0.8	0.5	2.3	−4.4	11.2	0.85	0.88	0.63	0.58	0.99	0.97
70	100	Esso aviation oil 100	−0.8	−11.5	−12.2	−6.5	−9.1	−9.9	−12.1	−1.14	0.95	0.92	0.60	0.77	0.88	0.90

[a] BRT No. 7. [b] Bardol. [c] Lot B.

CELLULOSE and CELLULOSE PLASTICS



The following six papers were presented in a symposium on this subject before a joint session of the Division of Cellulose Chemistry and Division of Paint, Varnish, and Plastics Chemistry at the 108th Meeting of the American Chemical Society in New York, N. Y. (The photographs show views in Hercules Powder Company's ethylcellulose plant at Hopewell, Va.)

THE behavior of cellulose and its derivatives during spinning and casting operations and the ultimate properties of films and filaments produced from them depend in an intricate manner upon the molecular properties of the material used in their manufacture. In the first place, the average molecular weight or polymerization degree serves to characterize a given high-polymer substance, has great influence on the viscosity of its solution, and is of primary importance for the mechanical properties of the final material. The number average molecular weight can be obtained by osmotic pressure measurements or by the chemical determination of end groups; the weight average by light scattering (*6*) or sedimentation velocity measurements; a still higher average, the so-called *z*-average is obtainable from sedimentation equilibrium runs in the ultracentrifuge. Viscosity measurements as such do not lead to a direct, absolute determination of any of these average values; but after appropriate calibration with carefully fractionated samples, they can be useful in obtaining the viscosity average molecular weight, the magnitude of which is usually somewhere between the number and weight average and, in some cases, is slightly above the latter. Many polymers such as polystyrene, polyisobutylene, rubber, starch, cellulose acetate, etc., permit the application of all or most of the absolute methods, such as end group determination, osmotic pressure, light scattering, and ultracentrifuge. In such cases the same sample was investigated by several methods, and fairly close agreement obtained between values based on independent observations. The viscosity method was then calibrated with fractionated samples and can be used for obtaining molecular weights or polymerization degrees of fractions and for estimating the viscosity average of unfractionated samples.

Cellulose in cuprammonium, cuprioxide ethylenediamine, or viscose offers considerable difficulties to the end group, osmotic pressure, and light scattering methods, and no reliable values for either fractionated or unfractionated samples have yet been reported. The only absolute method applied to cellulose itself is the ultracentrifuge. Stamm (*38*) and Lansing and Kraemer (*24*) measured the sedimentation velocity of unfractionated cuprammonium solutions of three samples of natural and two samples of regenerated cellulose, and used them to calibrate the viscosity method on the basis of Staudinger's rule. Recent extended studies, carried out in Svedberg's laboratory by Mosimann (*29*), Gralén (*16*, *17*), and Jullander, Ranky, and Snellman (*40*) seem to call for a revision of this calibration and, therefore, lead to new numerical values for the degrees of polymerization of natural and regenerated cellulose. This will be discussed more thoroughly in the second section of this article.

Another important fundamental feature of a polymer is its molecular weight distribution. It has long been known that most natural and synthetic high polymers represent a mixture of molecules having different degrees of polymerization. This polymolecularity can be detected by ultracentrifuge (*41*) and light scattering (*7*, *9*, *10*) measurements, and makes it possible to split a high-polymer sample into a number of fractions. Cellulose and its derivatives have been fractionated for several years (*31*, *32*, *33*, *37*), and recently this method was perfected for cellulose acetate by Harris and co-workers (*35*, *36*). Fractional precipitation, based on slight differences in solubility, is used to separate the species with different chain lengths from one another. The fractions obtained although not homogeneous are distinctly sharper than the starting material. They can be used to study the solubility characteristics of high polymers and the importance of polymolecularity for the spinning of fibers and casting of films, as well as for the ultimate mechanical properties of commercial materials. The section on "Fractionation of Cellulose Acetate" gives a few recent measurements taken in close connection with the work of Harris, Rutherford, and Sookne (*36*).

A third property of fundamental interest is that most organic high polymers, particularly cellulose and its derivatives, seem to consist of more and less highly ordered areas. Extensive studies of many authors using x-rays, optical methods, swelling, chemical reactivity, etc., have shown that the proportion order-disorder can and does vary over a wide range, depending upon what polymer (rubber, cellulose, nylon) is being investigated and what treatment the material has been subjected to before investigation. The actual situation can be expressed in various ways: One can speak of small crystallites or crystallized domains, embedded in an amorphous or disordered matrix (*28*); but it must be kept in mind that probably there is a gradual transition from a highly ordered area to an adjacent area of complete randomness through intermediate domains of intermediate degrees of organization. The situation has also been expressed by saying that the crystallites have no sharp or well defined surfaces, but that some chains are protruding from them like fringes or frays, forming domains of more amorphous or disorganized structure. An oriented polymer sample, such as a stretched fiber or rolled film, can also be considered as a system of parallelized long-chain molecules with certain imperfections in their mutual arrangement which can occupy larger areas and represent the disordered element of the total structure (*23*). Experimental evidence seems to be in favor of one of these qualitative pictures in one case, of another picture in another case. At present interest is not concentrated so much on a more précise description of this situation but rather on better experimental methods to determine quantitatively the order-disorder proportion in a given sample. The last section of this article describes a few measurements of the degree of accessibility or penetrability of cellulose fibers and an attempt to correlate them with previous studies of the crystalline-amorphous character of such systems (*26*).

CELLULOSE MOLECULES IN DILUTE SOLUTION

The conversion of the intrinsic viscosity, $[\eta]$ (*20*), of a cellulose solution in cuprammonium into degrees of polymerization is usually carried out with the aid of Staudinger's rule:

$$DP = K_t\,[\eta] \tag{1}$$

Kraemer recommends for K_t the value of 260, which is about 25% larger than the original tentative value of 200 given by Staudinger (*21*). Lansing and Kraemer (*24*) verified Equation 1 and calibrated K_t over a fairly wide range of *DP* with unfractionated samples. Unfortunately cellulose in cuprammonium does not lend itself easily to osmotic pressure observations and also offers difficulties for light scattering measurements. Direct check of the viscosity-average *DP* values as computed by Equation 1 was, therefore, impossible, and the values obtained were considered the best available, tentative *DP* scale for natural and regenerated cellulose (*27*).

RECENT PROGRESS in CELLULOSE CHEMISTRY

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Recent progress is reported in the field of cellulose and its derivatives in three respects: (1) the size and shape of cellulose molecules in dilute solution, (2) the polymolecularity of cellulose acetates; and (3) the existence of more or less easily accessible areas in bulk cellulose, particularly in fibers. The first and last items are apparently closely related to important mechanical properties of films and fibers made from cellulose or cellulose derivatives, such as ultimate tensile strength and elongation to break. They seem to be particularly important for the so-called transversal properties, such as resistance to folding, bending, and shearing, but they influence other important technical qualities such as moisture regain, swelling, dyeing, softness, and luster. The second point appears to be of interest for the behavior of spinning and casting solutions, particularly for the degree of orientation and crystallinity which can be expected if such solutions are subjected to certain coagulating and stretching operations.

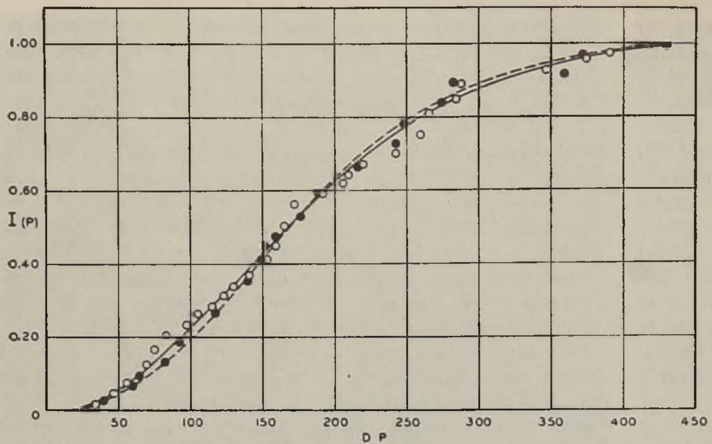

Figure 1. Integral Weight-Distribution Curves of Cellulose Acetate by Two Methods

There were, however, a few indications that these values might be too low. The K_i constants for polymers of the rubber type, such as rubber and neoprene, were on the whole larger (3400 for rubber in ether, 2000 for neoprene in *n*-butyl chloride) than for cellulose in cuprammonium. For example, the values of the intrinsic viscosities of rubber (*DP* 1000) in diethyl ether and cellulose (*DP* 1000) in cuprammonium are 0.3 and 4.0, respectively. This indicates that a cellulose chain in solution exhibits a viscosity about twelve times that of a rubber chain of the same *DP*. (Incidentally, these chains have the same maximum length when completely stretched.) While it is reasonable that a cellulose chain should be much stiffer than a rubber chain, a factor of twelve seems somewhat large. Another inconsistency arises from consideration of the *DP* values of the cellulose, before and after nitration. The *DP* of a cellulose sample in cuprammonium, as calculated from a K_i value of 260, is much less than the *DP* obtained by an absolute determination (osmotic pressure) of the same sample after nitration. This increase in *DP* is not very probable, although several explanations have been offered for it. The inconsistency would disappear if the *DP* values of the original sample were much higher than those obtained from Equation 1 when K_i equals 260. Further, it seemed odd that solutions of natural cotton with a *DP* value around 3000, according to Equation 1, should show deviations from Newton's law, whereas solutions of other polymers having similar *DP* values, such as polystyrene or nitrocellulose, do not exhibit these anomalies at comparable concentrations.

Svedberg and Gralén (*16, 17, 41*) recently reported an important study of the *DP* of cellulose in various solvents. Gralén's complete thesis contains a detailed description of his experimental procedures and results (*16*). The investigation included eighteen samples of natural and regenerated cellulose ranging from raw flax fiber to β-cellulose having Staudinger *DP* values from 3400 to 40, thirteen samples of cellulose nitrate in the *DP* range from 2700 to 780, and six samples of cellulose xanthate of 530 to 150 *DP*.

The cellulose samples were dissolved in cuprammonium solution and subjected to the following measurements: sedimentation velocity in the ultracentrifuge, diffusion in an improved Svedberg cell (*39, 42*), sedimentation equilibrium in the ultracentrifuge, and intrinsic viscosity in a modified Heuser and Green viscometer (*19*). Sedimentation and diffusion rates of all samples were determined at various concentrations over the approximate range from 0.05 to 1.0 gram solute per 100 ml. solution; sedimentation and diffusion constants *s* and *D* were determined at four to six different concentrations within this range. They were then extrapolated to infinite dilution with the aid of the equations:

$$s = \frac{s_o}{1 + kc} \tag{2}$$

$$D = D_o(1 + k_1c) \tag{3}$$

The molecular weights of the samples were computed from the Svedberg equation:

$$M = \frac{RTs_o}{D_o(1 - V\rho)} \tag{4}$$

T = absolute temperature
R = gas constant
V, ρ = partial specific volume of dry solute and density of solvent, respectively

Extrapolated values s_o and D_o are used in Equation 4 instead of any actually measured value at a certain concentration. Because s_o is larger than any actually observed s and D_o is smaller than any actually measured D, the values for M obtained in this way are considerably greater than those used at present for cellulose.

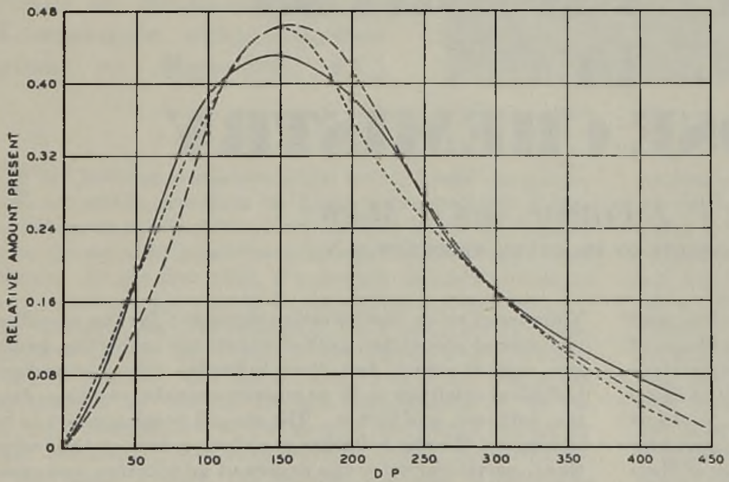

Figure 2. Differential Weight-Distribution Curves for Cellulose Acetate

Table I gives some of Gralén's measurements on various celluloses. Molecular weight and degree of polymerization in columns 6 and 7 (molecular weight of the cuprammonium complex of the monomer was assumed to be 226) were computed by Equation 4 with the extrapolated values of s_o and D_o as given in columns 3 and 5. Column 9 lists the *DP* values ascribed to these samples according to Equation 1 on the basis of intrinsic viscosity measured in the conventional way by extrapolation in the η_{sp}/c *vs.* c graph and listed in column 8. Comparison of columns 7 and 9 shows that the new *DP* values are considerably larger than the old ones, and that there is no simple proportionality between them. In fact, Gralén emphasizes that a *DP vs.* $[\eta]$ plot does not give a straight line. However, if the logarithms of the molecular weights (column 6) are plotted against the logarithms of $[\eta]$ (column 8), points are obtained which lead to the relation,

$$[\eta] = 8.5 \times 10^{-5} \times M^{0.81} \tag{5}$$

Table I. Summary of Graĺen's Data[a]

1 System	2 k	3 s_o	4 k_1	5 $D_o \times 10^7$	6 $M \times 10^{-3}$	7 DP	8 $[\eta]$	9 DP (Staudinger)	10 f/f_o	11 l_{max}	12 l	13 d	14 β
Cuprammonium solutions													
1. Raw cotton	9.0	10.4	7.0	0.20	2,400	10,800	12.6	2,520	9.8	60,000	10,700	18.9	0.68
2. Unbleached American linters	6.0	10.3	6.4	0.23	2,100	9,300	13.5	2,700	9.0	50,000	9,300	19.1	0.44
3. Normally bleached Am. linters	5.2	7.2	2.6	0.43	690	3,000	4.6	920	6.1	15,000	3,900	18.9	1.06
4. Chlorite-bleached Am. linters	6.9	9.2	5.0	0.26	1,700	7,300	7.7	1,540	8.6	40,000	8,100	18.1	1.04
5. Natural flax fiber	17.0	17.5	22.0	0.09	8,200	6,000	16.8	3,360	13.1	180,000	23,400	23.6	0.73
6. Natural nettle fiber	10.0	14.0	6.4	0.25	2,600	11,600	13.5	2,700	7.7	60,000	8,100	22.7	0.66
7. Natural ramie fiber	8.6	10.8	5.0	0.18	2,800	12,400	10.6	2,120	10.4	70,000	12,300	19.1	0.86
8. Sulfite pulp (97.1% alpha)	3.8	6.3	2.3	0.45	700	3,100	5.5	1,100	7.1	15,000	4,700	15.5	1.19
9. Sulfate pulp (94.6% alpha)	3.9	6.5	2.1	0.54	560	2,500	4.7	940	5.9	13,000	3,500	16.1	1.06
10. Aged alkali cellulose	1.1	3.8	0.6	0.84	210	940	2.3	460	5.3	5,000	2,200	12.6	1.59
11. Overaged alkali cellulose	0.2	1.9	0.9	1.54	62	270	0.6	120	4.6	1,400	1,200	9.1	1.94
Staple fiber (Phoix)													
12. From sulfite pulp	0.5	2.6	0.8	1.27	105	460	0.95	190	4.8	2,200	1,500	10.6	1.57
13. From sulfate pulp	1.7	4.1	2.2	0.66	320	1,400	2.1	460	6.4	7,500	3,200	12.7	1.24
Nitrocellulose in acetone, from													
14. Unbleached linters	4.2	19.0	4.2	1.00	780	2,700	..	...	12.2	14,000	9,800	11.3	0.38
15. Normally bleached linters	2.8	14.0	2.4	1.44	400	1,360	..	...	10.6	7,000	6,600	9.8	0.48
16. Chlorite-bleached linters	5.0	18.5	4.5	1.11	680	2,300	..	...	11.5	12,000	8,800	11.2	0.70
Nitrocellulose pulps													
17. Sulfate	3.5	16.2	5.6	1.56	420	1,450	..	...	9.6	9,000	5,900	10.8	0.82
18. Sulfite (89% alpha)	3.6	15.5	2.0	2.15	300	1,010	..	...	7.8	6,000	4,100	10.8	1.74
19. Sulfite (92.0 alpha)	4.8	16.7	3.6	1.94	350	1,200	..	...	8.2	6,500	4,600	11.1	1.33
20. Sulfite (94.1% alpha)	2.6	18.3	3.5	1.48	510	1,700	..	...	9.6	8,500	6,300	11.4	1.27
Viscose solution (alkali cellulose)													
21. Aged 48 hours	2.8	4.4	0.28	1.83	126	530	..	...	4.3	2,650	1,370	12.4	1.12
22. Aged 96 hours	0.7	2.4	0.0	3.40	37	150	..	...	3.4	750	660	9.6	1.04

[a] k and k_1 are computed for concentration, as grams of solute per 100 ml. solution; s_o is expressed in Svedberg units, D_o is given as sq. cm. per second. M refers to the copper cellulose complex, cellulose nitrate, and cellulose xanthate, respectively. DP (Staudinger) is computed with a K_m constant of 5×10^{-3}. $l_{max.}$, l, and d are expressed in Ångström units.

which should be used instead of Equation 1 to convert intrinsic viscosities of cuprammonium solutions of cellulose to molecular weights, M. The new values are considerably higher than those which have heretofore been assumed to be correct, particularly in the region of high DP (natural cellulose in various forms). The experimental data of Gralén are superior in quality and quantity to data used previously; their only shortcoming is that they were obtained with unfractionated samples. The evaluation of the measurements is based on standard procedures, except that viscosity of the solvent was used in the computation of sedimentation and diffusion constants s and D; Lauffer (*25*) pointed out that the viscosity of the solution leads to more logical and consistent results. In any case, the new data of Svedberg and Gralén (*16*) show that the present DP values for cellulose dissolved in cuprammonium are probably too small, and that the actual molecular weights of these materials are much larger.

Gralén (*16*) also determined sedimentation and diffusion rates and sedimentation equilibria for a number of cellulose nitrate samples and for some cellulose xanthates dissolved in sodium hydroxide. All investigated materials were unfractionated. Certain data obtained from sedimentation and diffusion velocity experiments (molecular weight and degree of polymerization computed according to Equation 4) are given in columns 2 to 7 of Table I. No intrinsic viscosity measurements are reported for these systems in Gralén's thesis, because it was only recently that Mosimann (*29*) made a thorough study of a number of cellulose nitrate fractions by coordinated viscosity and ultracentrifuge measurements. He found that the intrinsic viscosities of eight fractionated cellulose nitrate samples (12.2% N) which were prepared by Fivian (*11*) are correlated with their molecular weights as obtained from s_o and D_o by a relation of the form of Equation 5. His data lead to the values $K = 3.8 \times 10^{-6}$ and $a = 0.93$, and show that the Staudinger rule (Equation 1) does not hold exactly for the system cellulose nitrate in acetone (*12*). The exponent a, however, is not far from unity.

Table II. Average Effective Axis Ratios of Five Cellulose Nitrate Fractions Computed from Mosimann's Data

Mol. Weight	DP	Axis Ratio, l/d Completely stretched	Computed from sedimentation	Computed from f/f_o
613,000	2320	1083	320	290
199,000	750	352	210	188
80,200	300	140	140	144
30,000	113	53	60	57
6,200	26	12	15	16

Comparison of item 2 with item 14 of Table I seems to give a satisfactory answer to the question of whether native cellulose decreases or increases in DP during nitration. Unbleached linters (from American cotton) have a DP value around 2000 in cuprammonium solution; while the nitrate of similar linters in acetone exhibits DP value of only about 800. A similar drop in DP can be observed in other cases listed in Table I (compare items 3 and 15, 4 and 16, etc.). This eliminates the surprising result of a DP increase during nitration of natural samples, and reveals a moderate but distinct degradation which can be considered acceptable from the chemical point of view.

Another interesting result of Gralén's and Mosimann's work concerns the average effective shape of the dissolved polymer molecules in very dilute solutions. From their sedimentation and diffusion velocity data and their observation of the partial specific volume, V, and the dry density, ρ, of the solute, they compute the molar coefficient of friction, f, the frictional ratio, f/f_o, and the average effective axis ratio l/d of the dissolved macromolecules under the assumption of low degree of solvation. This axis ratio can also be obtained from s alone, if one follows Burgers' procedure (*3*), and Mosimann found that these two computations lead to rather closely agreeing values of l/d for fractions of nitrocellulose in acetone. Table II gives the results for five samples. The third column shows the axis ratio for completely stretchedout molecules, as they would be in a crystallized domain long enough to contain the whole molecule. Columns 4 and 5 give the average effective axis ratios of the unsolvated, ellipsoidal macromolecules from sedimentation constant s (according to Burgers) and from f/f_o (according to Svedberg). If one assumes that the individual particles in solution consist of randomly kinked chains with approximately free rotation about the bond between successive monomeric units, the axis ratio would be between 5 and 10. It is evident that the axis ratios as computed from the experimental data (s and f) are smaller than those of straight chains, but much larger than those of randomly coiled, completely flexible, linear molecules. The same conclusion can be drawn for all samples which Gralén investigated and becomes evident from a comparison of columns 10, 11, 12, and 13 of Table I.

This leads to the fact that the molecules of cellulose and its derivatives in dilute solution are neither completely straight nor tightly curled, but assume and maintain an intermediate shape of moderate undulation (*27*) which manifests itself by axis ratios as contained in Tables I and II.

There seems to be independent experimental evidence in the

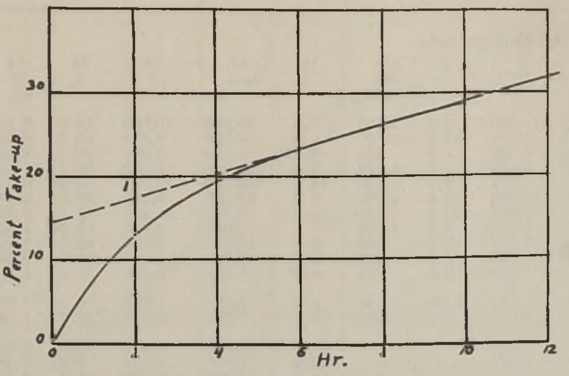

Figure 3. Take-up Rate of Water by Cellulose

same direction from intrinsic viscosity and light scattering. Simha (*34*) and Kraemer (*22*) pointed out that, under certain simplifying assumptions concerning the degree of solvation of the dissolved macromolecules, intrinsic viscosity can be used to estimate the average effective axis ratio l/d. Measurements with cellulose nitrate and cellulose acetate fractions in acetone and in acetone-methanol mixtures and observations with various polystyrene fractions lead to values of the same order of magnitude as those in Tables I and II, and confirm the comparatively stretched condition of these molecules in solvents of considerable solvation capacity.

Debye (*7*) recently worked out a quantitative theory to compute the relative spacious extension of macromolecules in dilute solutions from the dissymmetry of intensity of light scattered under various angles. Using his own data on polyvinylchloride and recent measurements of Doty (*8*) on vinylite fractions in cyclohexanone, polystyrene fractions in methyl ethyl ketone and toluene, and cellulose acetate in acetone, Debye arrives also at large axis ratios and hence at the conclusion of only moderately curled chain molecules in dilute solution.

FRACTIONATION OF CELLULOSE ACETATE

Sookne *et al.* (*35*, *36*) described a successful procedure to split commercial cellulose acetate (Eastman Kodak) into a large number of fractions by means of fractional precipitation. Considering the importance which polymer fractions are assuming in the theory of high-polymer solutions and in an understanding of the mechanical properties of films and fibers, it seemed worth while to try to reproduce Sookne's findings, using another commercial acetate (Du Pont) with similar characteristics.

Two fractionation techniques were utilized in these experiments. In the first, 250 grams of cellulose acetate (acetyl content 38.4%) were fractionated and refractionated from acetone solutions with ethanol as precipitant, according to the method outlined by Sookne, Rutherford, Harris, and Mark (*36*). Viscosity measurements were made on solutions of these fractions in methyl Cellosolve, and the relative degrees of polymerization were calculated from $DP = [\eta]/Kc$, where Sookne's K value of 9.7×10^{-4} was used.

A solution of the same concentration was used in the second method. Since suitable equipment of sufficient size was not readily available, only 50 grams of the acetate were fractionated. A 5-liter three-neck flask, containing 50 grams of cellulose acetate was set in a constant-temperature bath. Into the large central neck a tight-fitting stirrer was introduced through a glass tube which passed through a rubber stopper. A thermometer was inserted in one of the side necks. Acetone was added through the third neck so that a 2.5% solution of acetate resulted. The stirrer was connected to a variable-speed electric motor. With continuous rapid stirring, a quantity of ethanol (95%) was added until cloudiness resulted. Stirring was continued until it was certain that the cloudiness was not due to local action. Enough acetone was added to just clarify the solution again. The system was then just at the point of precipitation. The third side neck was connected to an aspirator through a suitable trap, which was turned on during rapid stirring. After 30–40 minutes the solution became cloudy. The suction action during this time caused no temperature drop within the flask. The aspirator was turned off, and stirring was continued for 30–45 minutes. When the stirring was stopped, fluffy flakes appeared which settled to the bottom of the flask in a short time as a gelatinous mass. If no settling occurred, the system was again subjected to vacuum action for a short time. The supernatant liquid was easily separated from the precipitate by decantation into another similar three-neck flask. The precipitate was removed after agitation with a suitable quantity of ethanol. This material was filtered through a Büchner funnel. This filtration had the advantage of removing the fine particles of the acetate which, particularly in the case of the lower-molecular-weight fractions, were suspended in the alcohol.

The supernatant liquor was subjected again to the above treatment, and the process was continued until no more fractions could be obtained. The remaining liquor was evaporated, and the fine powder obtained was considered to be the lowest fraction. The fractions were refractionated, as above, in a smaller flask; greatest attention was paid to the highest-molecular-weight fractions. The final fractions were dried in a vacuum oven at 55° C. for several hours and then weighed. Viscosity measurements were taken on solutions of the fractions in methyl Cellosolve, the degrees of polymerization were calculated as above, and fractions of similar DP were combined.

Figure 1 shows the two integral weight-distribution curves obtained with the same cellulose acetate by the two different experimental procedures. Each sample was split into about twenty-five fractions; in general, therefore, the curves can be drawn with fair accuracy and smoothness. They indicate that the two separation procedures lead to reasonably approximate results. Figure 2 represents three differential weight-distribution curves of cellulose acetate. Two of them correspond to the two integral curves of Figure 1, and the third is taken from the paper of Sookne *et al.* (*36*). The rather close agreement of the three curves may be taken as an indication of the reproducibility and reliability of the techniques employed. It may encourage a more widespread use of the fractionation of cellulose derivatives before they are investigated by the various physical and chemical methods discussed in the previous section.

ACCESSIBILITY OF HYDROXYL GROUPS

It was early recognized (*28*) that natural cellulose represents a composite structure consisting of crystallized and amorphous constituents; the belief was expressed that "the glucosidic chains, which are well oriented and parallelized in the interior of the crystallites, are getting more and more randomized as one approaches the surface of the micelles and are gradually going over into the amorphous matrix in which the crystallites are embedded". X-ray evidence qualitatively supports the existence of such amorphous and mesomorphous constituents; in the case of cellulose, however, it has not yet contributed any quantitative data about the ratio of ordered and disordered domains or the degree to which this ratio is affected by mechanical deformations during spinning, casting, or molding. It seems that careful measurements of the intensity distribution inside and between the crystal interference spots, as carried out by Baker and Fuller (*2*, *13*) and Gehman and Field (*14*) for other polymers, should open the way for more quantitative data about cellulose. Such measurements are in progress in I. Fankuchen's laboratory at the Polytechnic Institute of Brooklyn.

In the absence of reliable x-ray data, other methods have recently been used to obtain information about the presence of more or less highly ordered and, hence, more or less densely consolidated domains. In principle they all measure the rate of some process which takes place without destruction and, if possible, without change in the original texture of the sample. From the specific shape of the rate-time curve, certain conclusions are drawn as to the accessibility of the reacting groups if the process has gone to various extents. The rate of water regain and the rate of adsorption of organic vapors and dyestuffs show a distinct decrease at a certain point of take-up, which makes it probable that more or less accessible hydroxyl groups exist in a cellulose sample.

Quantitative methods for the determination of easily accessible areas have been proposed by Assaf, Haas, and Purves (*1*), Conrad and Scroggie (*5*), Goldfinger and Siggia (*15*), Harris and Purves (*18*), and Nickerson (*30*), by measuring the rate of a chemical reaction which does not destroy the texture of the sample up to high conversions. In most cases the take-up starts rather rapidly and, after a certain time, slows down to a zero-order process which continues over a long period. Figure 3 shows a typical conversion curve of this type. If, after a comparatively short initial steep portion, the curve flattens out to a long linear branch, it seems reasonable to consider the whole process as a superposition of a fast and a slow step, to evaluate the conversion curve by extrapolating the linear branch to zero time (broken line 1 in Figure 3), and to characterize the part of the material below the intercept of this line as the highly reactive or easily accessible component. This has led to the idea that, for many chemical reactions, certain fractions of the total material are more readily available than others; this idea has been expressed by various authors in terms of a certain percentage of amorphous or easily accessible domains. In natural cellulose, such as cotton, these fractions have been found to be between 2 and 15%, depending upon the individual nature of the sample and the method used.

It seems that the exchange of hydrogen with deuterium in the various hydroxyl groups of cellulose represents a particularly mild and smooth means of arriving at the amount of easily accessible areas in a given specimen. The hydrogen-deuterium exchange also has the advantage that it can be easily followed analytically and that it does not change the chemical nature of the original sample at all. Champetier and Viallard (*4*) showed that, after a sufficiently long time, all hydroxyl groups of cellulose exchange hydrogen with deuterium, an indication that the reaction takes place not only in the disordered, but also in the ordered domains. We have worked out a method of digesting cellulose in water of high deuterium content (around 50% D_2O) and, by taking samples of the liquid at various intervals, of determining the rate of hydrogen-deuterium exchange over a longer period and under different conditions of pH, temperature, etc. In all cases we obtained exchange curves with a steep initial portion and a long linear branch. Figure 4 shows the rate of exchange of a sulfite pulp sample.

The pulp (Rayocord wood pulp) was conditioned in an airtight jar for 48 hours. A 7-gram sample was then transferred to a 1-inch ground-glass stoppered test tube which contained 30.0 ml. of 37.11% D_2O. The tube was thermostated at 25° C. After an hour the pulp was disintegrated somewhat by manipulation with a wire; about 10 ml. of the water were then removed with a filter stick having a $^3/_4$-inch fritted-glass disk as the filtering unit. The water was distilled, and its specific gravity determined by means of a 10-ml. Ostwald-Sprengel pycnometer; the water was then returned to the test tube. This procedure was repeated every hour until the linear portion of the curve was well defined. A correction for the moisture content of the pulp must be made, the necessary data being obtained by a conventional moisture determination in an air oven.

It is evident from Figure 4 that there is a rather rapid hydrogen-deuterium exchange during the first hour, which slows down to a much lower rate thereafter. This indicates the existence of a two-step mechanism. There are, of course, several possible interpretations of this observation:

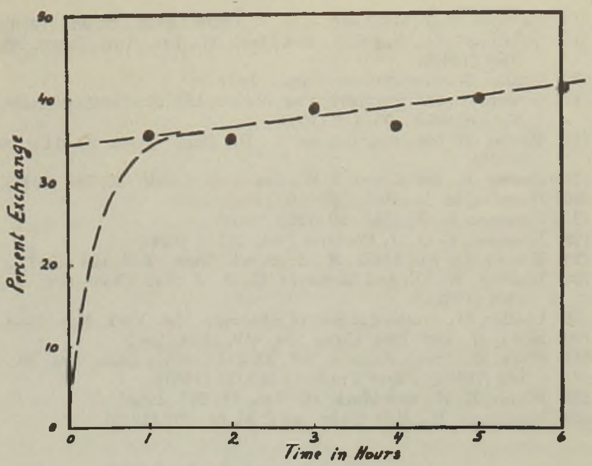

Figure 4. Rate of Hydrogen-Deuterium Exchange of a Sulfite Pulp Sample

1. One can assume that all primary hydroxyl groups of the cellulose, whether inside or outside of the crystallized areas, exchange much faster than all secondary hydroxyl groups and, therefore, are used up first. In this case the extrapolation of the slow zero-order exchange should intersect the ordinate at the point of 33% exchange.
2. One can assume that all hydroxyl groups in the disordered areas exchange much faster than all hydroxyl groups inside the micelles, in which case the extrapolated intersect on the ordinate would be proportional to the amount of amorphous or easily accessible material.
3. It is possible that all hydroxyl groups in the disordered areas and on the surface of the crystallites exchange fast.
4. It is conceivable that only the primary hydroxyl groups, which are easily accessible, exchange rapidly while all the others undergo slow reaction.

The extrapolation of the slow exchange in Figure 4 intersects the ordinate around 34% hydrogen-deuterium exchange, which would agree fairly well with assumption 1. It must be emphasized, however, that a more thorough investigation of the course of the exchange under various experimental conditions, such as pH, temperature, higher exchange ratios, etc., will be necessary before any definite statement can be made. Experiments along these lines are underway. At present we can only report that exchange rates of D_2O with the hydroxyl groups of cellulose have been measured and that they indicate the existence of a multistep reaction.

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WEATHER RESISTANCE OF Cellulose Ester Plastic Compositions

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A number of cellulose acetate butyrate and cellulose acetate plastic compositions were exposed for a period of two years to outdoor weathering in Arizona, Florida, and Tennessee. The effect on appearance and physical properties was studied. It was found that degradation is much less pronounced under more temperate climatic conditions. The resistance to weathering can be somewhat improved by the proper choice of plasticizer; it can be materially improved by adding small proportions of an ultraviolet light inhibitor such as salol. In the case of materials tested, the addition of an inhibitor is effective for both cellulose acetate butyrate and cellulose acetate compositions but is more effective for the former.

THE cellulose chain has the property of breaking down slowly when exposed to ultraviolet radiation. This accounts almost entirely for the development of brittleness in cellulose ester plastics on outdoor exposure (*9*, *10*). The short ultraviolet rays of the solar spectrum have been shown to have most rapid action (*4*). It has also been shown that the deterioration is accelerated by the presence of oxygen (*4*, *7*).

In addition to the development of brittleness, a certain amount of warpage usually occurs on outdoor exposure. The degree of warpage depends largely on the amount and type of plasticizer present in the molding composition (*1*, *2*). Least warpage is to be expected when the cellulose ester is compounded with little or no plasticizer or when it is plasticized with a material of low vapor pressure and low water solubility.

Recent investigations by Kline (*5*) at the National Bureau of Standards indicate that the breakdown of some plastics by ultraviolet radiation can be inhibited by the addition of a suitable organic compound such as salol (phenyl salicylate). Salol absorbs the ultraviolet rays and emits the resultant energy in some form not harmful to the surrounding material; it thus acts as a protective screen.

To obtain a practical comparison of the weathering characteristics of various cellulose-base plastics, a number of formulations were prepared and exposed to outdoor weathering tests at several localities. However, only the results of the cellulose ester compositions are reported here because we are most familiar with these materials. In the case of the other materials, only a limited number of formulations were tested and thus the resulting data might lead to erroneous conclusions.

EXPERIMENTAL PROCEDURE

Eight cellulose ester plastic compositions are reported. They are based on medium-viscosity cellulose acetate butyrate containing 14% acetyl and 37% butyryl, and medium-low-viscosity cellulose acetate containing 38.5% acetyl. The constituents of each composition are given in Table I. These compositions were processed by standard production methods and then granulated to $^3/_{16}$-inch particle size. Test panels 9 × 4 × $^3/_{16}$ inch were molded by compression under optimum molding conditions.

Outdoor tests were made at the following locations: Everglades Testing Laboratories, Fort Myers Beach, Fla.; Arizona Testing Laboratories, Phoenix, Ariz.; Tennessee Eastman Corporation, Kingsport, Tenn. The test panels were mounted on boards in such a manner that the plastic pieces were approximately $^1/_4$ inch off the surface. These boards were painted dull black. Exposure was due south at an angle of 45° to the horizontal. Samples were removed at intervals of 1, 2, 3, 4, 6, 8, 10, 12, 16, 20, and 24 months. All returned weathered samples were scrubbed with soap and water and then given a close inspection. The Arizona samples were covered with a light coat of dust and were easily cleaned. The Tennessee and Florida samples were covered with a more tenaciously adhering deposit and were therefore much harder to clean. This condition was aggravated by surface crazing. After inspection the samples were cut up and conditioned for testing.

Flow temperature, elongation, tensile strength, flexural strength and intrinsic viscosity were determined on the original and returned samples. As these tests were started in May, 1941, the test methods then used were different from the current A.S.T.M. methods. To correlate these data with tests started in May, 1942, these test methods have been continued.

Elongation and Tensile Strength. These two physical properties were measured simultaneously by a modification of A.S.T.M. method D48–37. Tests were run with a Tinius Olsen Universal hydraulic testing machine. Test specimens were cut to dimensions of 5 × $^1/_2$ × $^3/_{16}$ inch with the central portion ground down to $^3/_8$ inch width, and then were conditioned at 77° F. over anhydrous calcium chloride for 7 days. Specimens were clamped in jaws 3 inches apart and were tested at a crosshead speed of $^1/_2$ inch per minute. Elongation was measured as the amount of stretch at the instant of breakage and is reported in per cent of the original length. Tensile strength is the force required to break the test bar by extension.

Flexural Strength. A modification of A.S.T.M. method D48–37 was used. Test specimens were cut to dimensions of 5 × $^1/_2$ × $^3/_{16}$ inch and then conditioned at 77° F. over anhydrous calcium chloride for 7 days. Tests were run flatwise at a crosshead speed of $^1/_2$ inch per minute. Specimens were tested so that the maximum fiber stress in tension came on the weathered side.

Flow Temperature. A.S.T.M. method D569–43 was used to measure this property. Test specimens were cylinders of $^3/_8$-inch diameter piled up to $^3/_8$-inch height, and were conditioned at 77° F. over anhydrous calcium chloride for 7 days.

Intrinsic Viscosity. This property was determined by the method developed by Kraemer (*6*). The cellulose ester used was recovered from the returned weathered plastic samples. To obtain this material, it was necessary to dissolve the weathered plastic in acetic acid and reprecipitate the ester with isopropyl ether. The recovered sample was thoroughly washed with isopropyl ether to remove all traces of plasticizer and solvent and then dried overnight at 150° F. Intrinsic viscosity measurements were run on acetic acid solutions of this recovered material at concentration ranging from 1 to 3 grams per liter in a modified Ostwald viscometer at 25° C. The intrinsic viscosity was determined by graphical extrapolation of measurements made at different concentrations according to the Kraemer equation:

$$[\eta] = \left(\frac{\ln \eta_r}{c}\right)_{c \to 0}$$

where $[\eta]$ = intrinsic viscosity
η_r = viscosity of solution relative to that of solvent
c = concentration, grams solute/100 cc. solution

No attempt was made to calculate degree of polymerization from these data. The intrinsic viscosity measurements were taken as a comparative method of following the chain length breakdown.

OUTDOOR WEATHERING CONDITIONS

Before the weathering tests were started, it was known that the hot southern climates have a much more rapid and more serious degrading effect on cellulose ester plastics than the cooler northern climates. Therefore, only sites in the southern states were selected. Figure 1 compares mean temperature, per cent of possible sunshine, precipitation, and number of fogs on a monthly basis for Arizona, Florida, and Tennessee. These data were taken from U. S. Department of Commerce Weather Bureau reports compiled by weather bureau stations within 100 miles of the testing sites. They do not exactly represent the conditions during testing but are a close approximation.

Table I. Cellulose Ester Compositions

Constituents	Composition Number B1	B2	B3	B4	B5	A6	A7	A8
Cellulose acetate butyrate	100	100	100	100	100	...	...	...
Cellulose acetate	...	...	...	...	...	100	100	100
Dibutyl sebacate	...	...	13	12	7	...	...	...
Diethyl phthalate	...	...	...	...	...	42	48	36
Triphenyl phosphate	20	12	...	...	...	14	...	...
Salol	...	1	...	1	5	...	...	5

Arizona has the highest percentage of possible sunshine, the highest mean temperature with the greatest fluctuation between maximum and minimum, very little precipitation, and almost no fogs. Florida has an intermediate percentage of possible sunshine and mean temperature with the smallest degree of fluctuation between maximum and minimum, a relatively large precipitation, and a moderate number of fogs. Tennessee has the lowest percentage of possible sunshine, the lowest mean temperature but with fluctuations almost equivalent to Arizona, the greatest precipitation, and the highest number of fogs. Phoenix is located at latitude 33°30′ and 1100 feet altitude; Fort Myers Beach, at latitude 26°28′ and sea level; and Kingsport, at latitude 36°32′ and 1400 feet elevation.

The Arizona conditions probably include slightly higher concentration of ultraviolet radiation than the Florida conditions, even though the latter is at a more southerly latitude. This is due to the greater percentage of possible sunshine, the dryness of the climate, and the higher altitude. The Tennessee conditions include considerably lower concentration of ultraviolet radiation than either Arizona or Florida since the percentage of possible sunshine is lower than either and the location is at the most northerly latitude.

Another consideration having some importance but impossible to evaluate from available data is the effect of moisture content of the atmosphere and the altitude of the location on the wave length of ultraviolet light transmitted through the atmosphere. It is known that lower moisture content and higher altitude favor transmission of more short-wave-length ultraviolet radiation (*3*) which is more destructive to cellulose ester compositions (*4*).

EFFECT OF WEATHERING ON APPEARANCE

Samples in Arizona. Figure 2 shows the weathered samples Cellulose acetate butyrate compositions plasticized with dibutyl sebacate (B3) start crazing in 3 months in Arizona; however, on the addition of salol (B4, B5), there is only a slight dulling of the exposed surface in 24 months. When plasticized with triphenyl phosphate (B1), there is development of brittleness but no crazing until after 16 months; on the addition of salol (B2), the development of brittleness is stopped but dulling of the surface occurs in 20 months. None of the cellulose acetate butyrate compositions show appreciable warpage.

Cellulose acetate compositions plasticized with diethyl phthalate (A7) start crazing in 2 months in Arizona; on the addition of salol (A8), surface crazing starts in 8 months but is still confined largely to the surface at 24 months. When compositions are plasticized with diethyl phthalate–triphenyl phosphate (A6), crazing starts in 3 months. All of the cellulose acetate compositions show slight warpage after 2 or 4 months of exposure.

Samples in Florida. Figure 3 shows the weathered samples. Cellulose acetate butyrate compositions plasticized with dibutyl sebacate (B3) start crazing in 3 months in Florida; on the addition of salol (B4, B5), there is only slight dulling of the exposed surface in 24 months. When plasticized with triphenyl phosphate (B1), compositions start crazing in 12 months with the development of some brittleness much earlier; when salol is added, there is no development of brittleness and crazing starts in 16 months. None of the cellulose acetate butyrate compositions show appreciable warpage.

Cellulose acetate compositions plasticized with diethyl phthalate (A7) start crazing in 3 months in Florida; when salol is added (A8), surface crazing starts in 6 months but is still confined largely to the surface after 24 months. When the compositions are plasticized with diethyl phthalate–triphenyl phosphate (A6), crazing starts in 4 months. All of the cellulose acetate compositions show a slight warpage after 1 to 2 months of exposure.

The effects of weathering in Florida and Arizona are almost equivalent. The panels exposed in Florida were slightly more warped and more difficult to clean but started crazing after about

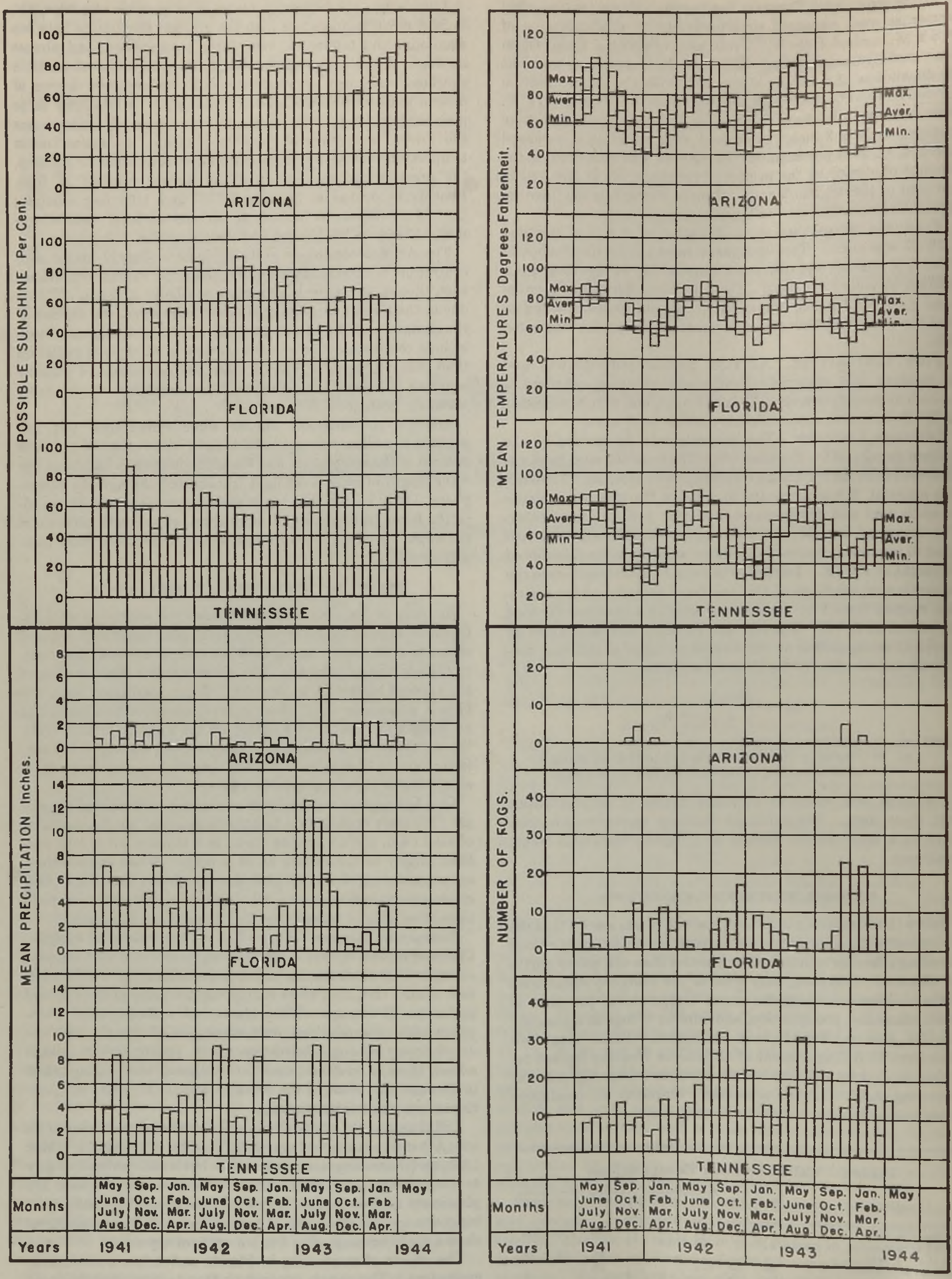

Figure 1. Possible Sunshine, Temperature, Mean Precipitation, and Number of Fogs during Weathering in Three Localities

the same exposure. Apparently the effect of the higher concentration of ultraviolet radiation and higher temperature in Arizona is balanced by the effect of greater precipitation and more fogs in Florida.

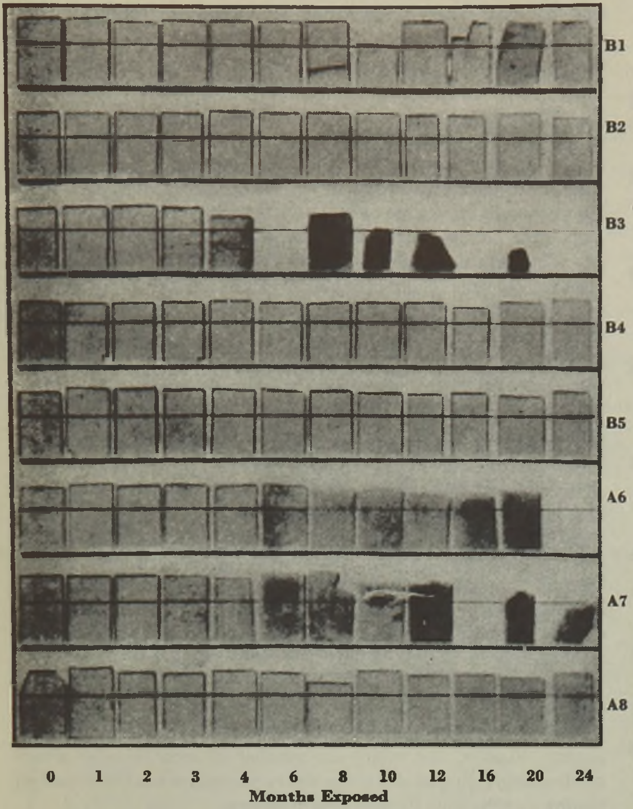

Figure 2. Appearance of Samples Weathered in Arizona

Samples in Tennessee. Figure 4 shows the weathered samples. Cellulose acetate butyrate compositions plasticized with dibutyl sebacate (B3) start crazing in 6 months in Tennessee; on the addition of salol (B4, B5), they are apparently unaffected in 24 months. When plasticized with triphenyl phosphate (B1), the material develops brittleness but no crazing in 24 months; it is apparently unaffected in 24 months on the addition of salol (B2). Very little warpage occurs in any of the cellulose acetate butyrate compositions.

Cellulose acetate compositions plasticized with diethyl phthalate (A7) start crazing in 4 months in Tennessee; on the addition of salol (A8), surface crazing starts in 6 months. However, as in the previous cases, little brittleness develops and the crazing is still confined to the surface at 24 months. When plasticized with diethyl phthalate–triphenyl phosphate (A6), the material starts crazing in 6 months. All of the cellulose acetate compositions show slight warpage after 2 to 3 months of exposure.

The effect of weathering in Tennessee is much less severe than in Arizona or Florida. This can be attributed only to the lower concentration of ultraviolet radiation since the amount of precipitation and number of fogs are greater than in Florida.

EFFECT OF WEATHERING ON PHYSICAL PROPERTIES

Before evaluating the physical data of the weathered samples, the accuracy of the test method must be considered. Under the best conditions plastic materials do not lend themselves to very precise physical measurement. Results on elongation, tensile strength and flexural strength are greatly influenced by the molding technique and by the smoothness of the test specimen surfaces. The panels for the tests started in May, 1941 (B1, B3, A6, and A7), were cut from large sheets compression-molded in an open-platen mold; the panels for the tests started in May, 1942 (B2, B4, B5, and A8), were cut from smaller sheets pressed in a positive-type mold. The molding technique was changed with the hope of obtaining less erratic results. However, the data on all weathered samples are more or less erratic because of the effect of surface imperfections induced by exposure. Therefore, the data are useful only in indicating trends and were plotted with that intent. Also shown is the time of exposure for the first appearance of crazing; the general type is indicated by *C* and the surface type by *D*.

Figure 5 shows the effect of weathering on tensile and flexural strengths. These properties can be discussed together since their behavior is almost identical. Compositions containing salol (B2, B4, B5, and A8) undergo little or no change in intrinsic viscosity over a 24 months' exposure. Cellulose acetate compositions containing salol (A8) surface craze in 6 months but salol confines this action to the surface as the strengths apparently suffer little degradation. Plastics containing triphenyl phosphate but no salol (B1 and A6) deteriorate at a slower rate than those plasticized with dibutyl sebacate (B3) or with diethyl phthalate (A7). All four compositions containing no salol breakdown appreciably before crazing.

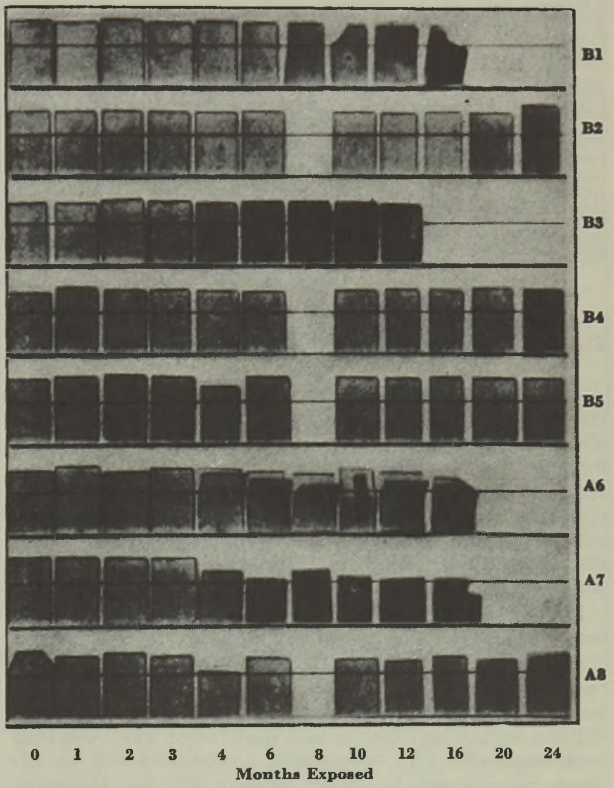

Figure 3. Appearance of Samples Weathered in Florida

Figure 6 shows the effect of weathering on flow temperature and intrinsic viscosity, which may be discussed together since their results are similar. These two properties are practically independent of mold technique and surface imperfections. The measurement of intrinsic viscosity is of fundamental importance. It has been shown that other physical properties are in large measure dependent on the chain length of the cellulose ester (*8*). Examination of Figures 5, 6, and 7 shows that a rough correlation does exist between breakdown of intrinsic viscosity and breakdown of other physical properties. However, intrinsic viscosity measurements are based on the entire sample and not on the weathered plastic surface alone. This surface forms only a thin slice of the thickness; hence the chain breakdown may not be apparent until the weathering has produced considerable degradation. These same considerations hold for the flow temperature. Where surface deterioration may affect other physical properties, it does not show up so quickly with these two properties. As with other physical properties, the addition of salol to cellulose acetate and acetate-butyrate plastics inhibits the breakdown of intrinsic viscosity and flow temperature beyond 24 months.

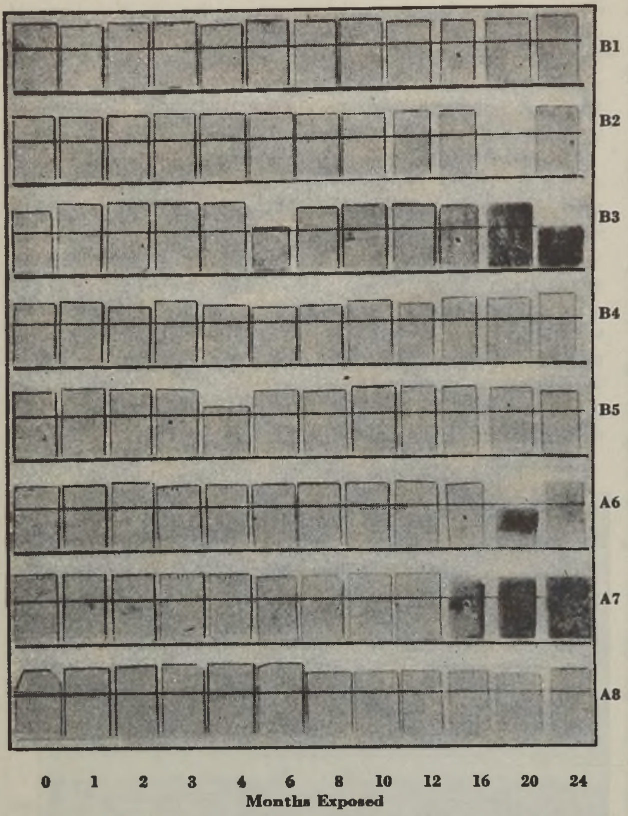

Figure 4. Appearance of Samples Weathered in Tennessee

Figure 7 shows the effect of weathering on elongation. These data are very erratic and therefore difficult to interpret. This is due in part to the technique employed in molding the original panels. Of equal importance, however, is the fact that elongation is very dependent on the quality of the test surface. The slightest surface imperfection may start failure which will then be propagated rapidly. Compositions plasticized with an aliphatic material such as dibutyl sebacate (B3) lose elongation rapidly just prior to the appearance of crazing. Compositions plasticized with diethyl phthalate (A7) behave similarly. Compositions plasticized with diethyl phthalate–triphenyl phosphate (A6) or triphenyl phosphate (B1) lose elongation at a lower rate but have reached the limiting value a considerable period before crazing occurs. This is especially noticeable with composition B1. Both cellulose acetate butyrate and cellulose acetate compositions containing salol (B2, B4, B5, and A8) retained approximately 50% of their elongation for 24 months. This fact shows conclusively that the crazing or dulling of compositions containing salol is almost entirely a surface phenomenon.

It is apparent that the most destructive of outdoor weathering conditions is ultraviolet radiation. The effect on cellulose ester plastics is breakdown of the cellulose chain, resulting in brittleness of the plastic as indicated by the rapid decrease in elongation of compositions containing no inhibitor. Moisture and temperature conditions also have considerable influence on the weathering characteristics of the plastics. In this case, however, degradation is caused by the effect on the plasticizer rather than the base material, and it results in warpage and gradual hardening of the surface. Results of excessive moisture are leaching of the plasticizer in proportion to its water solubility. High-temperature conditions result in the loss of plasticizer in proportion to its volatility and its degree of compatibility with the base material. Also, high temperature may contribute materially to warpage and sagging in the case of the softer compositions.

These considerations probably account for the early appearance of surface crazing in cellulose acetate compositions containing salol (A8). This composition is plasticized with diethyl phthalate which has higher solubility in water and is more volatile than any of the other plasticizers considered. These properties, together with the fact that the plasticizer is present in relatively large proportions (*1*), favor greater loss. This may also account for the greater warpage of all the cellulose acetate compositions.

In order to bring the relation between appearance and physical properties into better focus, Table II shows the number of months exposure to reach limiting values. The limiting value for tensile and flexural strengths has been taken as 50% of the original. Since both behave the same, only one set of figures is given. The limiting value for flow temperature has been taken as 250° F. and for intrinsic viscosity as [η] equals 0.75. Since these values are reached in approximately the same time, only one set of figures is shown. The limiting value on elongation has been taken as 50% of the original. The limiting characteristic on appearance has been taken as the first sign of crazing, however slight. Finally, the minimum number of months after which the limiting values of one of the above properties has been reached is shown as the time for first sign of failure.

CONCLUSIONS

The addition of a small amount of an effective ultraviolet inhibitor, such as salol, materially increases the weathering resistance of both cellulose acetate butyrate and cellulose acetate compositions.

Table II. Approximate Months of Weathering to Failure

	Cellulose Acetate Butyrate					Cellulose Acetate		
Composition Number	B1	B2	B3	B4	B5	A6	A7	A8
Arizona								
Tensile and flexural strength, lb./sq. in. (50% original value)	12	[a]	2	[a]	[a]	8	3	[a]
Flow temp. (drop to 250° F.) and intrinsic viscosity (drop to 0.75)	10	[a]	3	[a]	[a]	4	4	[a]
Elongation, % (50% original value)	4	[a]	1	[a]	[a]	2	1	[a]
Crazing (first sign)	16	[a]	3	24[b]	[a]	3	2	8[b]
Failure (first sign)	4	[a]	1	24	[a]	2	1	8
Florida								
Tensile and flexural	8	[a]	2	[a]	[a]	8	3	[a]
Flow temp. and intrinsic viscosity	6	[a]	3	[a]	[a]	8	4	[a]
Elongation	4	[a]	1	[a]	[a]	2	2	[a]
Crazing	12	[a]	3	24[b]	[a]	4	3	6[b]
Failure	4	[a]	1	24	[a]	2	2	6
Tennessee								
Tensile and flexural	24	[a]	4	[a]	[a]	24	4	[a]
Flow temp. and intrinsic viscosity	12	[a]	6	[a]	[a]	12	8	[a]
Elongation	12	[a]	2	[a]	[a]	3	3	[a]
Crazing	[a]	[a]	6	[a]	[a]	6	4	6[b]
Failure	12	[a]	2	[a]	[a]	3	3	6

[a] Greater than 24 months.
[b] Surface dulling, very shallow craze.

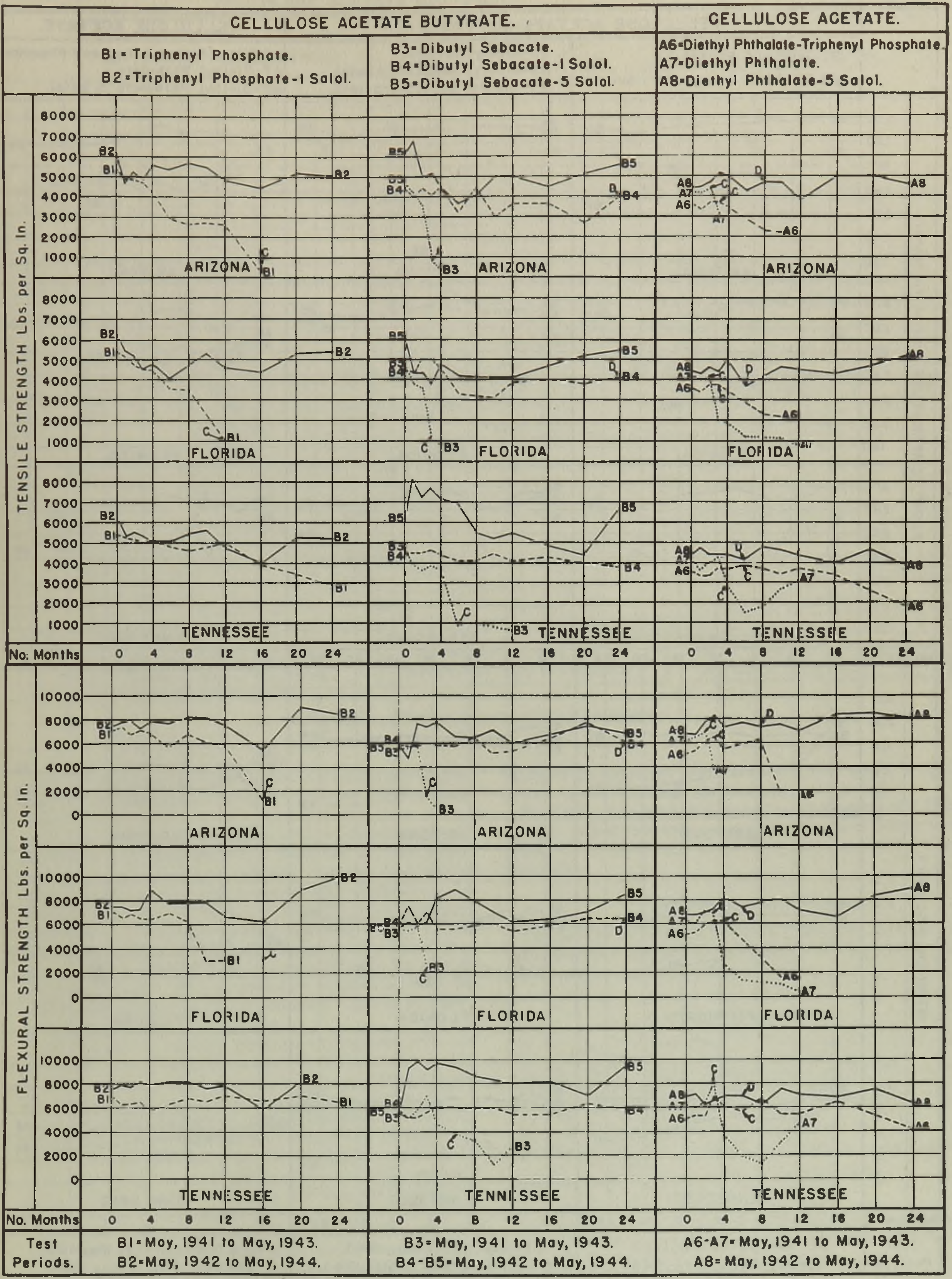

Figure 5. Effect of Weathering on Tensile and Flexural Strength

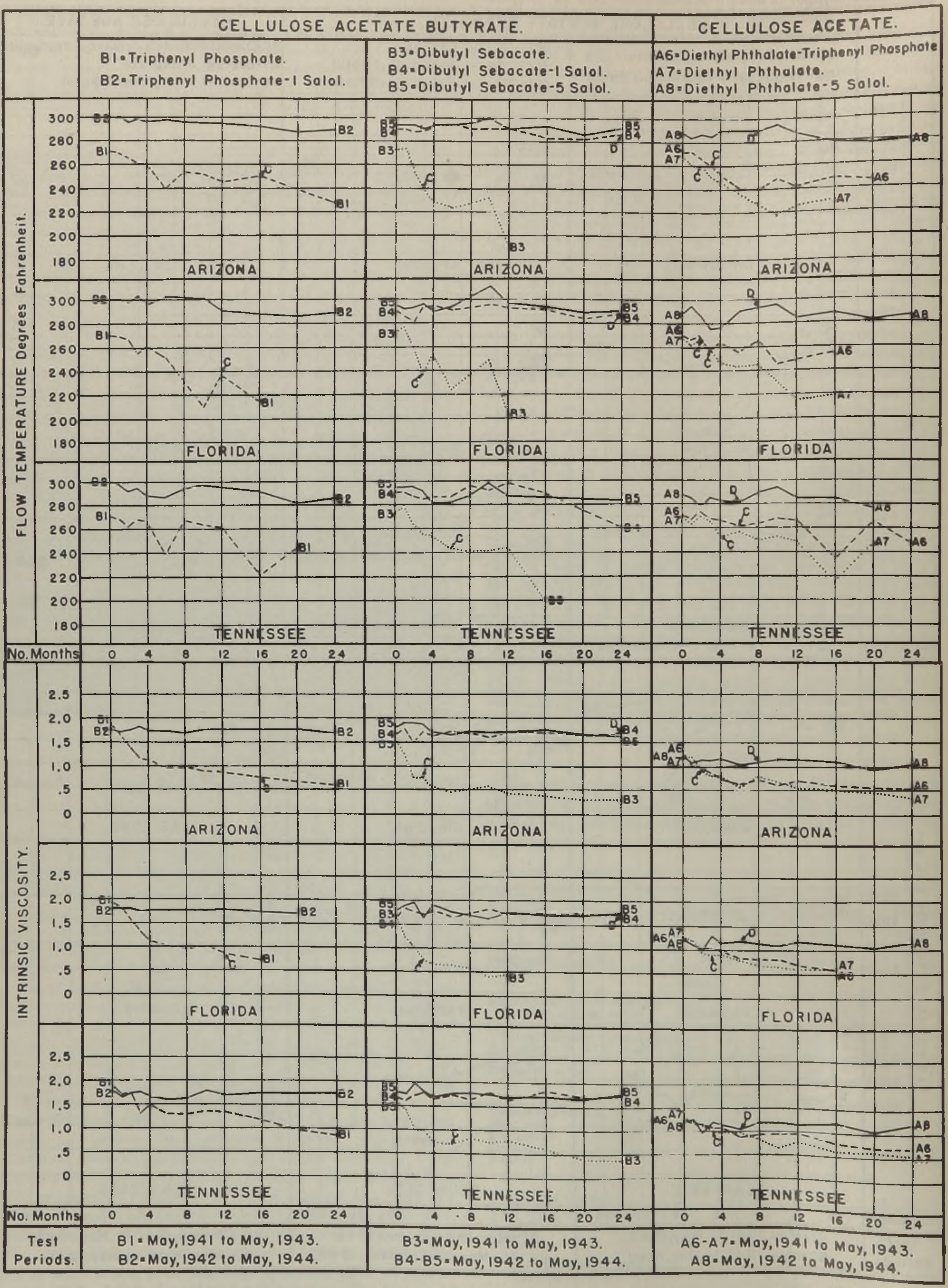

Figure 6. Effect of Weathering on Flow Temperature and Intrinsic Viscosity

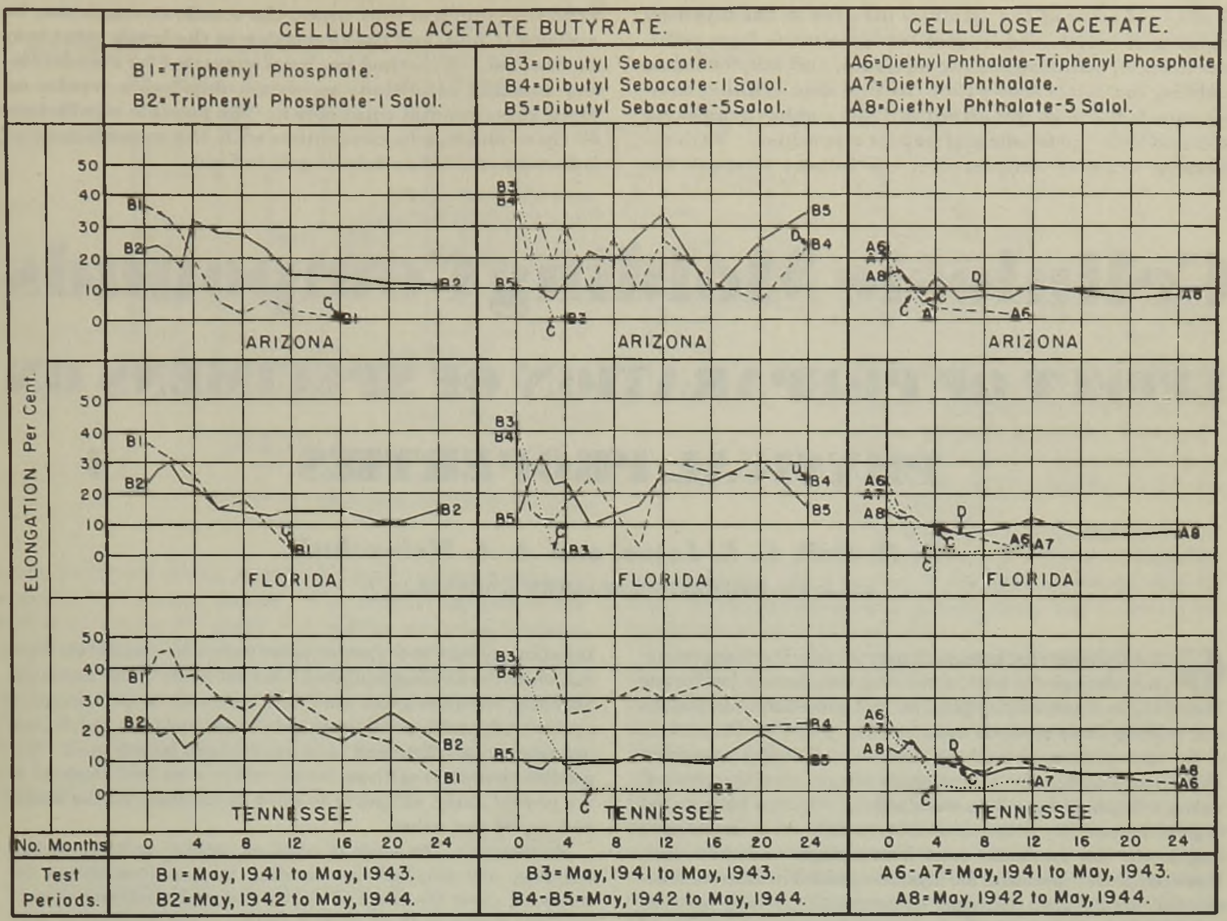

Figure 7. Effect of Weathering on Elongation

The effectiveness of the inhibiting action of salol is only slightly dependent on concentration down to 1 part per 100 of cellulose ester.

Cellulose ester plastics undergo at least two different types of degradation on outdoor exposure. These are the chain-length breakdown from ultraviolet radiation and the deteriorating effects caused by plasticizer leaching and volatilization. In plastics containing no inhibitor, the ultraviolet effect appears to predominate. The rate of breakdown depends largely on the ultraviolet concentration. The rate is considerably less in Tennessee than in Arizona and Florida and would be still less at more temperate climates. When an ultraviolet inhibitor is added, the second effect becomes the more dominant. This is especially noticeable in cellulose acetate plastics.

Cellulose acetate butyrate compositions containing salol are serviceable for more than 24 months in all test locations; the same materials without inhibitor fail in 1 to 4 months in Arizona and Florida, and in 2 to 12 months in Tennessee.

Cellulose acetate compositions containing salol have a tendency to warp and to develop slight surface crazing after 6 to 8 months of exposure but are serviceable from the standpoint of strength for more than 24 months in all test locations; the same materials without inhibitor fail in 1 to 2 months in Arizona and Florida, and in about 3 months in Tennessee.

A small but definite ultraviolet inhibiting effect can be obtained in cellulose ester compositions by choice of commercially available plasticizers. Triphenyl phosphate (an aromatic compound with three benzene rings) is better than diethyl phthalate (an aromatic compound with one benzene ring) which, in turn, is better than dibutyl sebacate (an aliphatic compound).

Since these data are based on continuous exposure in a fixed position subject to maximum sunlight, the life to failure is a minimum and considerably longer life would be expected of most applications.

ACKNOWLEDGMENT

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A study of some of the variables involved in the injection molding of tensile and impact test specimens from cellulose acetate, cellulose acetate butyrate, and ethylcellulose molding materials shows that the injection cylinder temperature is the most important variable and has a profound effect on both the tensile and impact test values. With increasing cylinder temperature, the impact strength increases as much as four times, the tensile strength may be reduced to half, and the elongation at the break point may be doubled. A method has been suggested for standardizing molding conditions to obtain duplicable results on given experimental equipment. The possible significance of these findings in connection with the manufacture of injection-molded articles is pointed out.

Cellulosic Molding Compounds

EFFECT OF PREPARATION OF SPECIMENS ON PHYSICAL PROPERTIES

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GREAT progress has been made over the past few years, principally through the work of the American Society for Testing Materials, in standardizing physical test procedures for plastics and making these methods more precise (*1–4*, *6*). Dimensions of the test specimens have been fixed. Conditioning procedures have been established. The methods of operating the physical testing equipment have been standardized. All this has resulted in good duplicability of test data between different laboratories as long as the test specimens come from a single uniform source. However, if test specimens are injection-molded in different laboratories, even though the same thermoplastic molding material is used, widely discrepant physical test values prevail, in spite of precautions taken in test procedure. These differences arise from variations in the method of preparing the test specimens, and are particularly prevalent in injection-molded specimens.

More than half of the production of cellulose plastics is converted into finished products by the injection method. It is always advisable to obtain test data under conditions closely related to those which prevail in the use of the material under test. This is particularly important in the case of injection molding because this method produces a structure in the molded piece which is not duplicated in any other molding method (*5*, *7*), and which is known to affect the physical properties of the molded part.

The injection molding process inherently possesses many variables, some of which are known to affect the strength of the molded part. The temperature of the injection cylinder which heats the plastic material, the injection pressure, the die temperature, the molding cycle, the diameter of the injection orifice, the rate at which material is injected into the die, the size and location of the gate, and the length of the runner are some of the variables encountered (*8*, *9*). In this paper a study is made of the effect of some of these variables on the impact strength and the breaking load and elongation in tension, as determined on a series of plastic molding compounds made from cellulose acetate, cellulose acetate butyrate, and ethylcellulose. The results show that the temperature of the injection cylinder is the most important of the variables studied, and profoundly changes the results of both the impact and tensile tests.

PROCEDURE

The primary injection cylinder temperature, the relation between the primary and secondary cylinder temperature, the molding cycle, and the die temperature were the variables studied. Injection pressure and injection speed were held constant throughout, since the molding equipment did not permit their variation. Similarly, since the molds used were built and in operation prior to this study, such questions as gate and runner size and die layout were already fixed and have not yet been investigated. It is possible that some of these factors which were held constant in the present study will prove to have an influence on the tensile and impact test values.

MATERIALS. The series of cellulose acetate, cellulose acetate butyrate, and ethylcellulose molding compositions chosen for this work cover the range of plastic flow and plasticizer content normally found in these three plastics. They were taken both from production lots of homogeneously plasticized and blended materials and from smaller similarly prepared experimental batches; in all cases common and commercially available plasticizers were used. The cellulose acetate formulations studied were from typical commercial production. The cellulose acetate butyrate compositions were experimental batches, one of which was compounded from commercial base flake (13.5% acetyl, 36.5% butyryl), and the others from a laboratory-synthesized flake of similar composition. The ethylcellulose materials were prepared from commercial flake. All samples were analyzed for plasticizer content and tested for A.S.T.M. flow temperature (*2*). The moisture contents of all materials were reduced to less than 0.5% by infrared drying prior to molding.

INJECTION MACHINE. A specially designed laboratory injection molding machine of 1-ounce capacity, operating through two hydraulic pistons, was used for all tests. This machine is shown schematically in Figure 1. Molding powder granules are fed through a hopper into the cylinder as indicated. Piston 1, actuated by a central hydraulic system, operates a 1$^1/_2$-inch-diameter injection plunger which provides 13,700 pounds per square inch injection pressure to force the plastic material through the injection cylinder. The latter is electrically heated by two collar-type resistance units which divide the heating cylinder into primary and secondary plasticization sections. The temperature of each section was controlled independently by rheostats to within ±2° F. and in most cases to ±1° F. Thermocouple wells are inserted in each heating zone for measurement of temperatures.

A spreader (torpedo) is located in the forward part of the main plasticization section to permit rapid and uniform heating of the material. The internal diameter of the cylinder is then tapered down to a tip having an orifice of about $^3/_{32}$-inch-diameter through

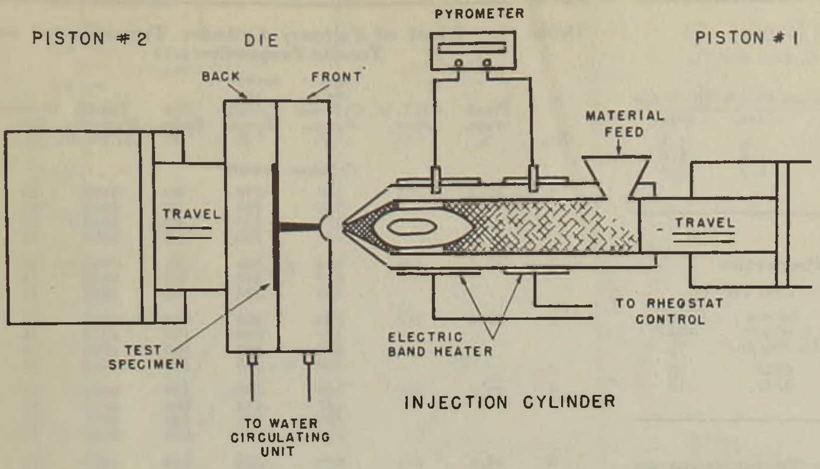

Figure 1. Injection Molding Machine

which the heated plastic material is forced into the die at each stroke of the injection plunger. The material capacity of the heating cylinder is 350 grams of a molding compound having a specific gravity of 1.29 and a compression ratio of 2.2.

Hydraulic piston 2 governs the opening and closing of the die, moves the closed mold up to the cylinder for filling, and supplies the necessary clamping pressure to hold the mold together during injection. The front half of the mold is fitted with a steel bushing which provides a seat for the cylinder tip. In order of operation the molding cycle in seconds is as follows:

	Impact Mold	Tensile Mold
1. Close mold	0	0
2. Move closed mold up to injection cylinder tip	1	1
3. Inject plasticized material	2	2
4. Withdraw injection plunger	14	10
5. Feed material into hopper	16	12
6. Withdraw mold from cylinder tip	35	20
7. Open mold	36	21
8. Remove molded piece	37	22
9. Close mold	45	30

The temperature of the plastic material is governed mainly by the primary cylinder temperature in this injection machine. A number of spot checks, taken after the machine had been in operation on cycle at a steady temperature for 20 minutes, have indicated that the temperature of the material leaving the nozzle is 8–10° F. below the primary cylinder temperature. The 600-watt primary heater (Figure 1) is located over the torpedo, at which point the plastic is in a thin cross section so that rapid and uniform heat transfer is obtained. The 400-watt secondary heater functions principally as a preheater for the material. Furthermore, with the impact mold the time required for complete passage of the material through the cylinder is 15 minutes. Because of the heater arrangements and the slow time cycle, the secondary heater contributes only slightly to the actual material temperature.

Specimens and Methods of Testing. The impact and tensile test specimens used in these studies were injection-molded in a highly polished, two-cavity, ported mold (Figure 2) with dimensions as indicated. The weight of material injected at each shot was 17.5 grams for the impact and 16 grams for the tensile mold. The die temperature was maintained at ±3° F. over the range 60–190° F. by circulating thermostatically controlled water through the mold ports at a rate of 2 gallons per minute.

For impact testing, the $^{1}/_{8} \times {}^{1}/_{2} \times 5$ inch molded bars were converted into Izod impact specimens by cutting a 2.5-inch-long piece from the center and notching it on a shaper to a depth of 0.100 inch according to A.S.T.M. standard D256–41T (*1*). Variations of 10% in the depth of the notch and a range of notching speeds from 160 to 440 inches per minute taking cuts of 0.005 inch depth, were found to have no effect on impact strength.

Both the equipment and method used for the impact tests were in accordance with A.S.T.M. standard D256–41T. At least fifteen and in many cases thirty specimens were used for each test.

For tensile tests the molded specimens were broken from the runner which leads the material into the die cavity, and no machining was required. The tensile properties were determined on ten specimens according to A.S.T.M. standard D638–42T (*4*), except for the dimensions of the test piece. This tensile mold was in operation prior to the adoption of the present standard A.S.T.M. tensile test piece.

All specimens were conditioned at 77 ± 3° F. and 50 ± 2% relative humidity prior to testing (*3*). The time of conditioning was at least 48 hours for tensile specimens (0.080 inch thick) and 72 hours for impact specimens (0.125 inch thick).

Duplicability. In the injection process, time is required for the material in the heating cylinder to reach temperature equilibrium with the cylinder. Similarly, time must be allowed for the die temperature to adjust itself after a change has been made. Therefore, the first essential in attaining duplicability is to operate the machine for a sufficient time to reach steady state after each change in molding conditions, before test specimens are collected. For the machine and molds used here, 15 to 20 minutes of steady machine operation are required before specimens of constant physical properties are obtained. This procedure was carefully followed throughout these studies, and test specimens were taken only after equilibrium conditions had been attained on the machine. Approximately thirty to sixty shots were taken for physical testing.

Table I shows typical duplicability of impact data on a cellulose acetate composition molded at the same conditions on three different dates. It also indicates that the molding procedure established for this work gives specimens with reproducible physical

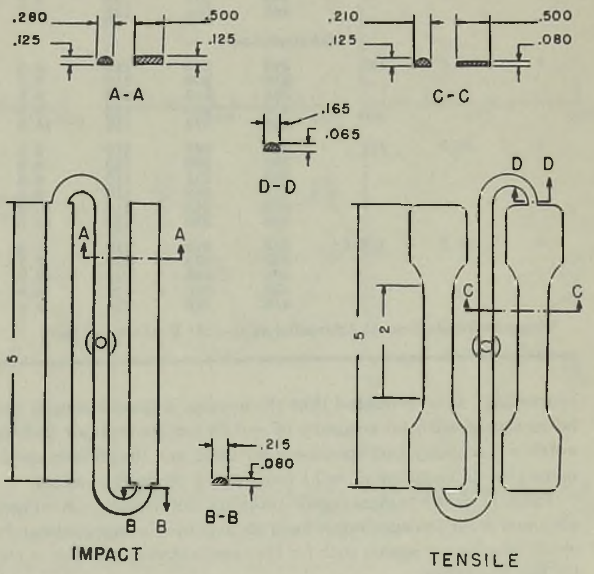

Figure 2. Diagram of Molds

Table I. Duplicability of Izod Impact

(Cellulose acetate, 22.1% plasticizer; A.S.T.M. flow, 163° C.)

Date	Cylinder Temp., ° F. Primary	Cylinder Temp., ° F. Secondary	Die Temp., ° F.	Izod Impact, Ft.-Lb./In. Notch Av.	Max.	Min.
7/3	402	332	145	1.6	1.8	1.3
7/5	402	332	145	1.6	1.8	1.0
7/6	402	332	145	1.7	2.2	1.2

Table II. Duplicability of Tensile Properties

(Cellulose acetate, 25.3% plasticizer; A.S.T.M. flow, 154° C.)

Date	Cylinder Temp., ° F. Primary	Cylinder Temp., ° F. Secondary	Die Temp., ° F.	Tensile Strength, Lb./Sq. In.	Elongation, %
8/17	425	355	125	6800	13
8/28	425	355	125	6700	13

Table III. Effect of Primary Cylinder Temperature on Izod Impact Strength

No.	Plasticizer, %	A.S.T.M. Flow, ° C.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Die Temp., ° F.	Izod Impact, Ft. Lb./In. Notch
Cellulose Acetate						
1	35.2	132	340	270	100	3.5
			355	280	100	4.7
			390	315	100	6.0
2	29.7	152.5	365	305	100	2.1
			395	320	105	2.8
			435	365	105	4.7
			468	405	105	6.2
3	23.5	165.0	395	325	100	1.3
			425	345	105	3.0
			460	365[a]	105	3.0
			495	375[a]	100	3.5
Cellulose Acetate Butyrate						
1	18.2	129	327	257	100	2.0
			355	285	100	4.9
			380	310	100	6.6
			405	335	100	7.8
2	11.2	146	363	293	120	1.4
			390	320	120	2.5
			415	345	120	3.3
			440	370	120	4.6
3	11.7	145	369	300	120	1.9
			390	320	120	2.1
			390	320	120	2.3
			410	340	120	3.5
			450	380	120	4.6
4	6.9	158	387	316	135	1.3
			415	345	135	1.8
			440	370	135	3.1
			465	395	135	2.9
Ethylcellulose						
1	15.1	143	345	275	110	3.5
			370	300	110	7.7
			395	325	110	9.3
			420	350	110	9.9
			445	375	110	11.3
2	19.7	141	335	265	110	2.9
			360	290	110	8.3
			385	315	110	9.8
			410	340	110	9.4
			435	365	110	10.0
			460	390	110	11.0
3	24.7	128.5	315	245	110	4.8
			340	270	110	7.7
			365	295	110	8.9
			390	320	110	8.9
			415	345	110	9.4

[a] Machine limitations set differential at 95–125° F. at time of test.

properties. It is estimated that the average impact strength can be measured with an accuracy of ±0.03 foot-pound per inch of notch when thirty test specimens are used, and that fifteen specimens give an accuracy of ±0.1 foot-pound per inch of notch.

Table II shows typical tensile property duplication. Averages obtained from ten specimens have an accuracy of approximately ±150 pounds per square inch for the tensile strength and of ±1% for the elongation.

Table IV. Effect of Primary Cylinder Temperature on Tensile Properties

No.	Plasticizer, %	A.S.T.M. Flow, ° C.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Die Temp., ° F.	Tensile Strength, Lb./Sq. In.	Elongation, %
Cellulose Acetate							
1	37.6	125	340	270	90	5100	23
			350	280	90	4400	22
			380	310	90	3100	25
			400	330	95	3000	32
2	30.2	134	355	285	90	7900	16
			380	310	90	5800	13
			405	335	90	4800	16
3	29.4	147	385	315	100	6400	18
			410	340	100	4900	18
			435	365	100	4700	20
			460	390	100	4200	26
4	28.3	151	400	330	125	6000	18
			427	355	125	4600	20
			450	380	125	4700	22
			475	405	125	5000	23
5	25.4	153	400	330	125	8900	15
			425	355	125	6800	13
			450	380	125	6000	15
			475	405	125	6100	14
6	23.2	163	415	345	125	8900	15
			440	370	125	6500	14
			465	395	125	6100	16
Cellulose Acetate Butyrate							
1	18.2	129	350	277	95	6400	33
			375	305	95	4300	26
			400	330	95	3300	30
2	11.2	146	385	315	120	8100	22
			410	340	120	5400	21
			435	365	120	4800	23
			460	390	120	4700	34
3	6.9	158	408	338	135	11000	29
			435	365	135	7300	22
			460	390	135	4800	22
			486	414	135	5100	26
Ethylcellulose							
1	24.7	128.5	340	270	110	3100	13
			365	295	110	2800	14
			390	320	110	2500	26
			415	345	110	3100	25
2	19.7	141	368	298	110	4700	13
			393	323	110	4200	14
			418	348	110	3900	18
			443	373	110	3800	22
3	15.1	143	368	298	110	4600	10
			393	323	110	4000	13
			418	343	110	3700	15
			443	373	110	3800	21
			468	398	110	4300	21

EFFECT OF PRIMARY CYLINDER TEMPERATURE

In any study of the molding temperature range in injection molding, a primary consideration is the determination of the "cold point" or minimum injection cylinder temperature at which the molding cycle can be successfully maintained without running into short samples (that is, incomplete filling out of the mold cavities). The existence of such a cold point is common to the injection molding of all thermoplastic materials, although the cold point temperature of a given compound will vary with the injection molding machine and die construction used. While this minimum molding temperature has no significance from a commercial viewpoint, it does serve to fix the lowest point in the molding temperature range and is a characteristic property of the molding composition used. With a given machine and mold and with variables other than molding temperature held constant, the cold point of a molding material is easily duplicable within 1 or 2° F.

Effect on Impact Strength. Representative groups of cellulose acetate, cellulose acetate butyrate, and ethylcellulose molding compounds were molded into impact test pieces while the primary cylinder temperature was varied over the maximum molding temperature range for each compound. A 45-second cycle was used throughout, and the die temperature was held constant for the molding of each composition. Because of the

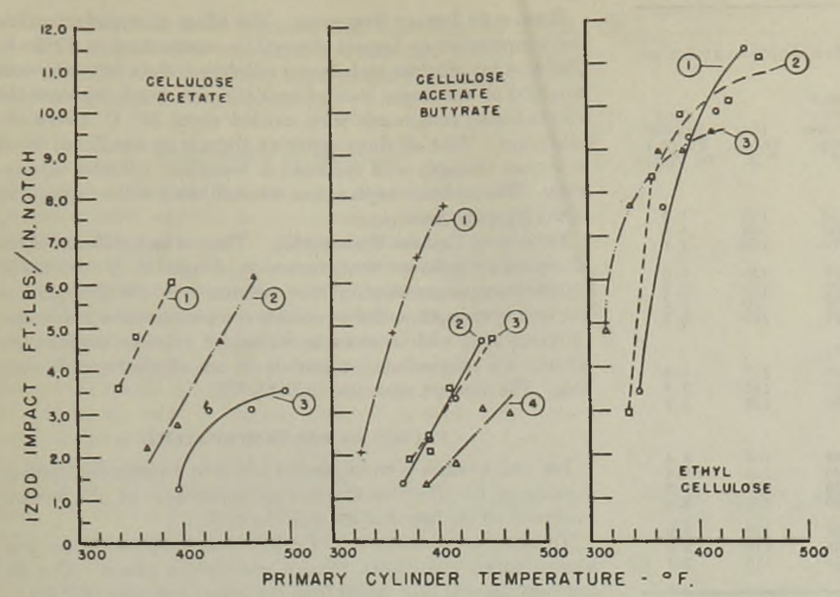

Figure 3. Effect of Primary Cylinder Temperature on Izod Impact Strength

operating characteristics of this machine, and particularly because heat conduction from the primary to the secondary zone makes it difficult to hold the secondary cylinder temperature constant while raising the primary over the range used here, a constant differential of 70° F. between the primary and secondary temperatures was maintained in this series of experiments.

The first group of test specimens was taken at the cold point. The temperatures were then raised in steps of 15° to 30° F., and samples for determination of physical properties were taken at each temperature step after the establishment of steady-state conditions. This process was repeated up to practical molding limits (i.e., where bad flashing or discoloration occurred). The molding temperature range varied from 50° to 135° F., ethylcellulose and hard cellulose acetate showing the greatest molding range, and cellulose acetate butyrate and soft cellulose acetate the smallest. The impact results are given in Table III and Figure 3; it is evident that the impact strength of these three cellulosic plastics is a function of the primary cylinder temperature, increasing greatly with increasing temperature.

It may be argued that the temperature range used in these experiments was extreme and would never be duplicated in good molding practice. However, there is a substantial temperature range with every injection machine which gives moldings that neither are cold-molded nor show flashing. At some point within this range the molder fixes his cylinder temperature, based on experience. Within this good molding range for the injection machine used in these studies, the increase in impact strength was usually at least 50% and was characteristic of all three plastic materials tested.

Effect on Tensile Properties. The same general procedure was employed. The primary cylinder temperature was raised stepwise from the cold point, with the secondary cylinder temperature 70° F. lower; other variables were held constant. A 30-second molding cycle was used, which is standard for the tensile mold with this injection machine. The molding range was found to be limited to about 75° F. maximum above the cold point, which is considerably less than in the case of the impact mold. The results are summarized in Table IV. The effect of primary cylinder temperature on tensile strength and on elongation is shown in Figure 4.

The tensile strength decreases with increasing cylinder temperature, dropping to 60% for cellulose acetate and 50% for cellulose acetate butyrate, expressed as per cent of the cold point values. With ethylcellulose there was some indication of a minimum, and the difference between maximum and minimum was much less.

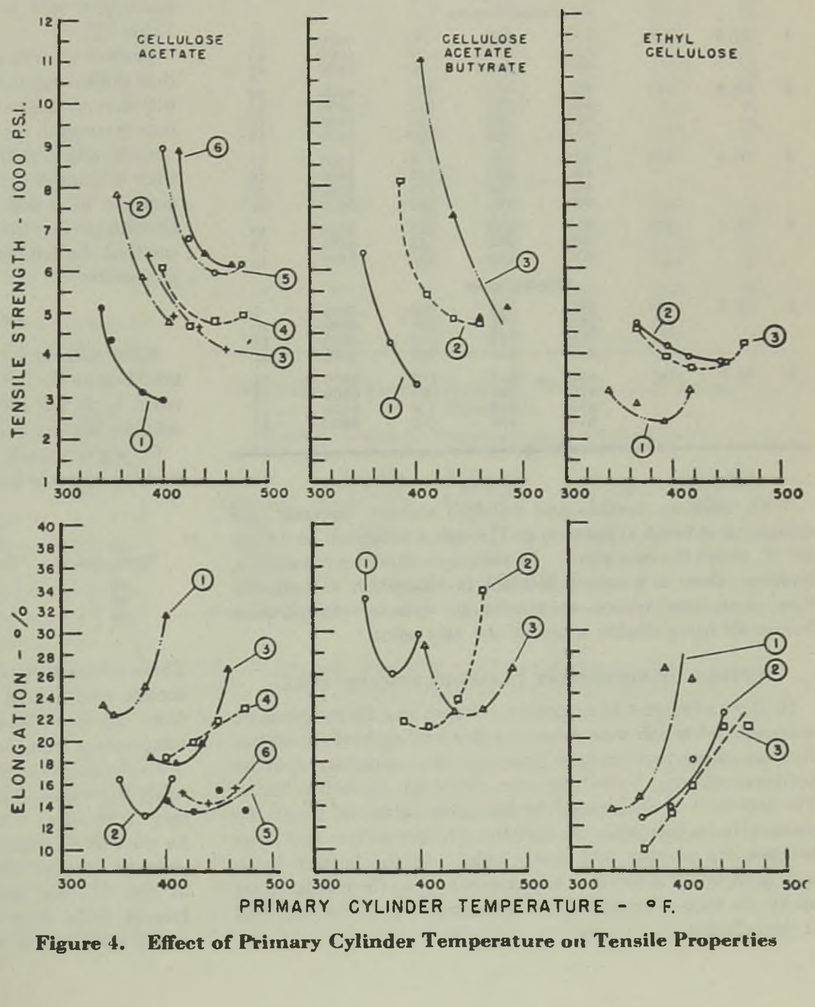

Figure 4. Effect of Primary Cylinder Temperature on Tensile Properties

Table V. Effect of Secondary Cylinder Temperature on Impact Strength

No.	Plasticizer, %	A.S.T.M. Flow, ° C.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Die Temp., ° F.	Izod Impact, Ft.-Lb./In. Notch
			Cellulose Acetate			
1	22.1	163	402	332	145	1.6
			402	352	145	1.5
			402	377	145	1.7
2	29.1	152	377	307	120	2.0
			377	327	120	2.2
			377	352	120	2.2
			377	377	120	2.2
			Cellulose Acetate Butyrate			
1	11.7	146	390	290	120	2.8
			390	320	120	2.3
			390	350	120	2.7
			Ethylcellulose			
1	22.0	128.5	365	265	100	8.4
			365	295	100	8.4
			365	325	100	8.2
			365	350	100	8.4
2	13.7	147	426	326	110	2.2
			426	386	110	2.2
			426	411	110	2.1

Table VI. Effect of Secondary Cylinder Temperature on Tensile Properties

No.	Plasticizer, %	A.S.T.M. Flow, ° C.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Die Temp., ° F.	Tensile Strength, Lb./Sq. In.	Elongation, %
			Cellulose Acetate				
1	37.6	125	350	280	90	4400	23
			350	310	90	4000	23
			350	340	90	3600	21
2	29.4	147	405	305	120	6200	19
			405	335	120	5500	18
			405	365	120	5400	19
			405	395	120	5200	19
3	28.3	151	403	301	125	5800	17
			400	329	125	6000	18
			400	360	125	5300	17
			400	390	125	5400	17
4	25.4	153	400	330	125	8900	15
			400	360	125	8500	13
			400	390	125	7500	14
			Ethylcellulose				
1	21.0	131	365	265	100	3900	9
			365	295	100	3900	10
			365	325	100	4000	11
			365	350	100	4000	11
2	13.7	147	415	315	110	6400	11
			415	345	110	6500	11
			415	375	110	6400	11
			415	400	110	6400	11

With cellulose acetate and cellulose acetate butyrate the elongation at break appears to go through a minimum at 15° to 25° F. above the cold point. In the ethylcellulose compositions, however, there is a steady increase in elongation as temperature rises, the values at maximum cylinder temperature frequently being double those at the cold point.

EFFECT OF SECONDARY CYLINDER TEMPERATURE

In these experiments a primary cylinder and die temperature were selected which were known to give well-molded specimens. Keeping these temperatures constant, the secondary cylinder temperature was varied between practical operating limits. The top limit is determined by the temperature at which the material in contact with the injection plunger softens and flows between the plunger and the cylinder. At the bottom limit, lack of injection pressure is encountered due to the resistance set up by the mass of unplastified molding material in the back half of the cylinder.

Effect on Impact Strength. The effect of secondary cylinder temperature on impact strength is summarized in Table V. The data for cellulose acetate and cellulose acetate butyrate were obtained on specimens molded near the cold point, whereas the ethylcellulose compounds were molded about 50° C. above the cold point. With all three materials there is no significant trend in impact strength with variation in secondary cylinder temperature. The probable explanation was indicated in the description of the injection machine.

Effect on Tensile Properties. There is no significant effect of secondary cylinder temperature on elongation in the case of cellulose acetate or ethylcellulose compositions. With regard to the tensile strength, cellulose acetate compounds show a decrease of about 20% with increase in secondary cylinder temperature whereas the ethylcellulose materials are not affected by this variable. The data are presented in Table VI.

EFFECT OF DIE TEMPERATURE

Die temperature is an important factor in commercial molding because of its effect on the surface appearance of the molded piece and on the length of the molding cycle.

To study this point a set of cylinder molding conditions was chosen which was known to give well-molded pieces. The die temperature was then raised from the lowest available (60° F.) to the highest point which allowed the molded pieces to be removed from the die without undue distortion. This top temperature was approximately 175° F.

Effect on Impact Strength. Although some changes are noted in the values, they are of small magnitude and follow no definite trend either for cellulose acetate or ethylcellulose. The conditions used and the results obtained are summarized in Table VII.

Effect on Tensile Properties. Data in Table VIII show that the change in elongation with change in die temperature is within experimental limits. There is also no significant change in tensile strength for either cellulose acetate or ethylcellulose compounds, although the variation in some of these values is greater than estimated experimental error and might indicate a slight decrease in tensile strength with increase in die temperature. Despite the fact that the results are somewhat erratic, it is apparent that die temperature has no significant influence on tensile properties.

EFFECT OF MOLDING CYCLE

Since commercial molders generally operate injection molding machines on the fastest molding cycle which will give good molded parts, cycle was investigated with the impact mold and a single cellulose acetate molding compound.

On a given machine, the minimum molding temperature is dependent upon the molding cycle as the following cold points show:

Cycle, Sec.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Die Temp., ° F.
35	395	325	145
45	392	322	145
55	388	318	145

These values were obtained on the impact mold using a cellulose acetate composition of 22.1% plasticizer and 163° C. A.S.T.M. flow. As the molding cycle is shortened, the minimum molding temperature increases.

To eliminate the effect of temperature on impact, and to study solely the relation between cycle and impact strength, it is necessary to mold at a comparable point in the moldable range for each cycle chosen. This was accomplished by taking the primary cylinder temperature at 10° F. above the cold points, at the 35-, 45-, and 55-second molding cycles, respectively. Impact data were obtained as given in Table IX. These values indicate a slight increase in impact strength with increased cycle, but it is apparent that variations of ±22% from the standard 45-second molding cycle have only a slight effect upon the Izod impact strength compared with the effect of variations in cylinder temperature.

DISCUSSION OF RESULTS

The temperature of the molding material as it leaves the injection cylinder appears to be the main factor affecting the strength of the molded part. The rate of cooling during the solidification of the plastic in the mold, which is largely governed by die temperature, has little effect on strength properties. In the molding machine used in these experiments, the temperature of the plasticized material is governed chiefly by the primary cylinder temperature, as pointed out previously. At each injection the tensile die takes 16 grams every 30 seconds, and the impact die takes 17.5 grams every 45 seconds, of the 350 grams of material in the injection cylinder, so that approximately 15 minutes are required for the material to pass through the cylinder. The material is traveling through the cylinder so slowly that it has time to reach temperature equilibrium with the primary heating zone where the main heat input occurs. For this reason neither the molding cycle nor the secondary cylinder temperature was found to have much effect on strength. This would probably not be the case if the mold took a major part of the cylinder capacity at each injection. It should, therefore, be borne in mind that any molding variable which affects the temperature of the molding material entering the die will undoubtedly affect the strength of the molded part.

This research is being continued and the scope broadened to study other thermoplastic molding compounds, the effect of molding conditions on other physical properties, and the problem of correlating physical tests between molding machines of different capacity and design. However, enough has been learned from this preliminary investigation to indicate the importance of the problem.

As far as impact and tensile values on injected-molded specimens of the cellulosic plastics are concerned, it is already apparent that the variation produced by changes in molding temperature over the normal molding range is so great that the figures have significance only if the molding conditions are specified. This is particularly serious when figures from one laboratory are compared with those obtained in another.

Within a single laboratory this difficulty can be overcome by carefully standardizing injection molding conditions with relation to the A.S.T.M. flow temperature of the compound. By arbitrarily selecting a standard molding temperature at a suitable level above cold point, all compounds are molded at a comparable point in their moldable range, and a true comparison between them is obtained regardless of their difference in flow. With the three types of plastics under discussion in this paper, a direct relation has been found between the cold point and the A.S.T.M. flow temperature. It is therefore possible with these materials to calculate a standard molding temperature from a determination of the A.S.T.M. flow temperature. By establishing molding temperature in this way, and standardizing the other injection variables, reliable data are obtained from injection-molded test specimens. This procedure has been established in this laboratory by selecting a primary cylinder temperature 45° F. above the cold point for the tensile and impact dies, using the injection machine described here.

The problem of obtaining duplication between one molding laboratory and another is a more formidable task than standardization within a given laboratory. To obtain such correlation it would be necessary for each machine and mold used for the injection of test pieces to be studied and calibrated in a manner similar to that reported here. The proper relative point in the molding temperature range would then have to be selected, based on the testing of a number of standard compounds which would have to be made available for wide distribution from a uniform stock. Such a program would be a large undertaking and would have to be sponsored by a suitable national organization. However, since the major portion of the thermoplastic molding material production is manufactured into finished goods by the injection method, it is highly desirable that specimens for physical tests should also be molded by injection.

Table VII. Effect of Die Temperature on Impact Strength

No.	Plasticizer, %	A.S.T.M. Flow, ° C.	Die Temp., ° F.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Izod Impact, Ft.-Lb./In. Notch
			Cellulose Acetate			
1	37.6	125	75	363	293	5.4
			100	363	293	5.2
			125	363	293	5.2
			150	363	293	5.0
2	25.3	154	75	420	350	2.3
			100	420	350	2.6
			125	420	350	2.6
			150	420	350	2.6
			175	420	350	2.5
			Ethylcellulose			
1	22.0	128.7	70	365	315	8.6
			90	365	315	8.2
			125	365	315	8.6
			150	365	315	9.0
2	13.7	147	60	426	356	2.2
			125	426	356	2.3
			150	426	356	2.3
			175	426	356	2.4

Table VIII. Effect of Die Temperature on Tensile Properties

No.	Plasticizer, %	A.S.T.M. Flow, ° C.	Die Temp., ° F.	Primary Cylinder Temp., ° F.	Secondary Cylinder Temp., ° F.	Tensile Strength, Lb./Sq. In.	Elongation %
			Cellulose Acetate				
1	29.3	147	60	405	335	6200	22
			95	405	335	5600	21
			120	405	335	5500	18
			150	405	335	5300	20
2	28.3	151	90	400	333	5700	18
			120	400	329	6000	18
			145	400	328	5700	16
			175	400	330	5700	15
			100	450	380	4600	21
			125	450	380	4700	22
			145	450	380	4700	22
3	23.1	162.5	100	438	368	7300	16
			125	438	368	7200	16
			145	438	368	7300	15
			170	438	368	7400	16
			Ethylcellulose				
1	22.0	128.5	60	365	295	3800	10
			90	365	295	3900	10
			115	365	295	3800	11
			140	365	295	3800	11
			165	365	295	3400	13
2	13.7	147	65	415	345	6600	11
			95	415	345	6400	11
			125	415	345	6200	11
			150	415	345	6400	11

Table IX. Effect of Molding Cycle on Izod Impact Strength

(Cellulose acetate molding compound 1, 22.1% plasticizer; A.S.T.M. flow, 163° C.)

Cycle, Sec.	Primary Cylinder Temp.,[a] ° F.	Secondary Cylinder Temp., ° F.	Die Temp., ° F.	Izod Impact, Ft.-Lb./In. Notch
35	405	335	145	1.5
45	402	332	145	1.6
55	398	328	145	1.7

[a] Molding temperatures taken at 10° F. above cold point.

In addition to their bearing on physical testing, the results observed here are probably also reflected in the strength values and utility of manufactured goods injection-molded from the cellulosic plastics. It has long been recognized that cold-molded pieces have poor strength, but the results recorded here indicate that the effect is even broader, and that large variations in strength must be expected within the range of normal molding temperatures. This presents the molder with an additional problem in determining and controlling his molding conditions, but it also gives an additional tool which may be used to accentuate certain desirable properties in the molded part.

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Interchain Order and Orientation in CELLULOSE ESTERS

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Study of the molecular, fine structure of cellulose derivatives as affected by their composition and fabrication is the purpose of this report. Other papers in this symposium show effects of composition and fabrication on physical properties and utility. Thus, in conjunction with these data, and by work yet to be reported, the fundamental connection between the habits of the chain molecules and the mechanical and electrical properties of finished plastics is further established. Molecular arrangement, as indicated by x-ray diffraction, has been investigated in various cellulose esters and mixed esters. The first part of the paper reflects operations such as extrusion, molding, cooling, and cold working during processing of any cellulose plastic; the latter part treats chain substitution and plasticizer as variables in the fine structure. A brief comparison of starch and cellulose esters emphasizes differences between polymer structures with the same empirical formula.

VARYING perfection of ordering or packing of chain sections in solid cellulose esters results from suitable treatment with heat, solvents, or hydrogen-bonding agents (*2*, *7*). Physical properties of these thermoplastics are accordingly affected, within a given chemical composition, by factors during molding or film formation which determine the final molecular order. Enhanced toughness and capacity for elongation, for example, are favored by less perfect order. These phenomena are apparently general for all linear polymers.

A study of these principles is extended here, using x-ray diffraction, to the following specific states of cellulose esters and mixed esters: (*a*) oriented, as in fibers, rolled films, or extruded sections; (*b*) plasticized, either by internal disorder from partial or mixed substitution, or by added plasticizers.

PREPARATION OF MATERIALS

Fibers and films of the most ordered polymers, cellulose triesters, and an acetate butyrate containing 2.2 moles of acetyl and 0.6 mole of butyryl per mole of pyranose rings, were made from materials previously described (*7*). The other cellulose mixed esters fell in a similar range of viscosities. Most of them were kindly provided by Eastman Kodak Company whose analyses of composition are quoted in the discussion. From these analyses, other properties may be derived (*24*).

Samples of pure flake and pressure moldings from it were used, the latter providing a starting point for fiber and sheet formation. In several instances the original flake was extracted or roughly fractionated and re-examined, to establish that degradation products such as cellobiose derivatives were not contributing to the structures observed.

Heat and solvent treatments were carried out as previously described (*7*). Fiber orientation was usually effected by drawing, at 150–200° C., films cast from solvent such as chloroform. These were cast so that they were not oriented by shrinkage during drying. Other filaments and strips were oriented by extrusion from the molten polymers. Unoriented sheets or fibrous sections were usually rolled at room temperature. Extrusion and rolling were found to simulate closely effects found from examination of actual injection moldings. Samples containing plasticizer were likewise made up from solution and carefully dried.

The fine structure resulting from a given treatment of a sample was generally characterized by x-ray diffraction diagrams. These were obtained by established techniques (*2*, *7*). Measurements of the longer spacings were checked on diagrams from monochromatic x-rays reflected from a pentaerythritol crystal. Optical birefringence was occasionally measured as a rapid and sensitive check on the direction of changes induced by heat or mechanical effects. Comments on standard physical properties are made on the basis of usual laboratory tests.

CONCEPT OF CHAIN ORDER

Fundamental effects of local chain order on physical properties of cellulose derivatives are intimately connected with longer range order, or orientation, possessed by the sample. By "local chain order" is meant the mutual arrangement of chain sections extending only throughout the volume of a single crystallite or micelle—i.e., of relatively few chains. We may assume that, even when these regions are ordered, fringes between them remain disordered, although this is not certain.

Polymers disordered locally by quenching or other means can generally be oriented most readily, contrasted to those initially highly ordered or crystallized (*12*). Similarly, while close control of the temperatures and times in a molding cycle may uniformly produce a given state of local order in a molding, the manner of molding, shape of the mold, etc., may cause more or less molecular orientation. This is an additional and important variable in assessing the physical qualities of the product.

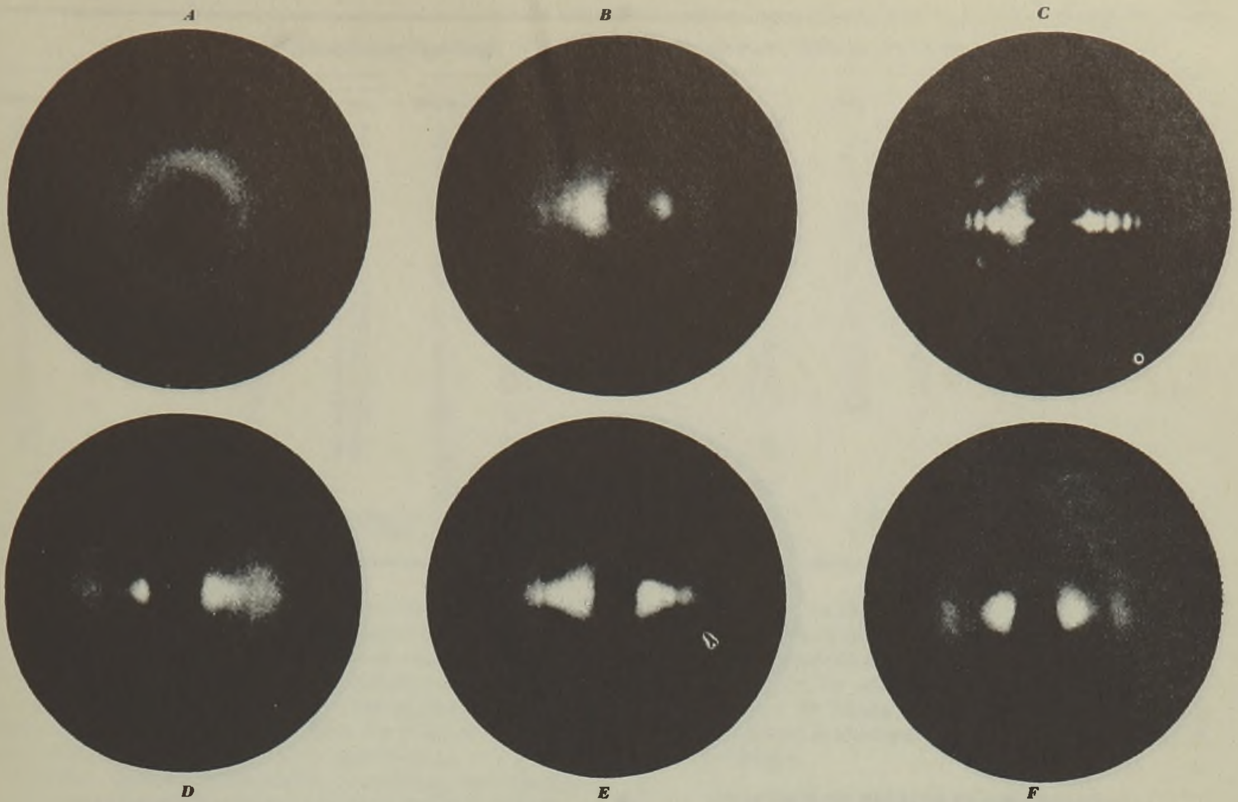

Figure 1. X-Ray Patterns of Oriented Cellulose Esters, with Fiber Axis Vertical

Rolled cellulose triacetate with (A) beam perpendicular to plane of rolling, (B) beam parallel to plane of rolling; cellulose acetate butyrate (C) drawn uniaxially and annealed, (D) rolled after drawing and annealing, with beam perpendicular to plane of rolling; (E) same sample and position after final annealing; (F) sample rolled and then drawn as in (C), beam perpendicular to original plane of rolling.

The occurrence and recognition of varying states of local order existing in different orientations (of the chains with respect to the boundaries of the sample) will first be shown. Examples used are typical polymers of such composition that precise interchain organization, or crystallinity, can eventually be reached. Some examples in which incomplete substitution or added plasticizer limits the attainable local order will also be noted.

It appears that the complex literature on the structure of cellulose esters and other derivatives can be greatly simplified by the concept of a continuous range of states of local chain order rather than of certain definite polymorphic forms such as cellulose acetate I, cellulose acetate II, etc. True polymorphism, which can exist in high polymeric systems (for example, the high-temperature *vs.* low-temperature forms of crystalline polyamides), has been confused, especially in the foreign literature, with the incidence of metastable states (*2*, *7*).

ORIENTATION

Familiar uniaxial fiber structure, one class in Weissenberg's system (*46*) of anisotropy in solids, was early noted in cellulose triacetate (*17*). However, other classes, which occur more commonly in molding and forming of present-day cellulose derivatives, were later obtained by working cellulose hydrate filaments (*16*), and films (*10*) and drying bacterial cellulose (*25*). Moreover, it is possible to produce in derivatives of cellulose, at least to some degree, all of the classes of orientation found in native cellulose itself. A thorough study of these classes in cellulose, with terminology which will be adopted here, was reported by Sisson (*37*).

Thus, despite early negative attempts to obtain higher orientation in cellulose esters (*40*), selected drying conditions of cellulose acetate and cellulose nitrate films, cast from solvent, caused (optical) anisotropy (*23*) similar to the effects of mechanical working shown below. McNally and Sheppard (*23*) noted that x-ray studies by Trillat confirmed the indications of higher orientation from birefringence (*40*, *43*). Further, varieties of orientation other than uniaxial fibering are now known to be possible generally in synthetic linear polymers (*4*, *9*, *30*).

It is therefore evident that interpretation of physical properties of cellulose esters in terms of fine structure must be attended by knowledge of both local chain order and orientation within the sample as a whole.

ORIENTATION BY COMPRESSION (ROLLING). For example, sheets of cellulose esters rolled to half their initial thickness, compression-molded at low temperatures, or injection-molded under suitable conditions, exhibit enhanced resistance to tearing. Tearing is known to be difficult across the long axes of chain molecules, compared to directions of stress which tend to pull them apart laterally. It would seem that the molecules had been arranged so that few segments along their long axes were normal to the plane of the sheets. Rather, it appears that most of the long axes lie randomly distributed in the sheet plane—i. e., with uniplanar orientation. Actually, severe pressing such as usually occurs in practice also causes some preferred positions around the long axes of the crystallites, so that selective uniplanar orientation, or ring fibering, might be found.

This effect appears in patterns *A* and *B* (Figure 1) for a sheet of cellulose triacetate rolled to about 30% of its initial thickness. *A*, taken normal to the plane of rolling, shows missing features from preferred orientation around the major axes of crystallites, random orientation of the long axes, and diffuse lines, largely because of the moderate local order of the original sheet cast from chloroform (*7*). *B*, taken parallel to the plane of rolling, affirms the restriction, approximately to a plane, of the long-

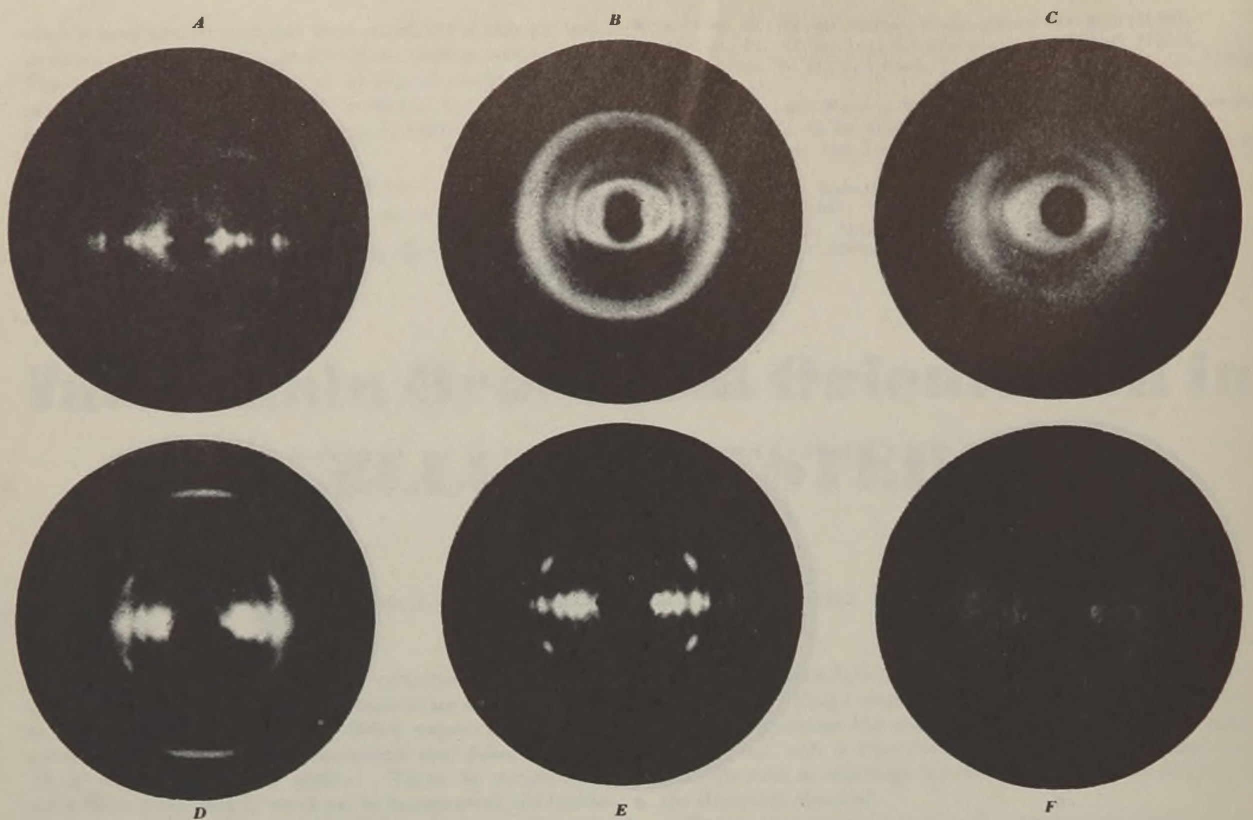

Figure 2. X-Ray Patterns of Oriented Cellulose Esters, with Fiber Axis Vertical

Cellulose tributyrate (*A*) drawn uniaxially, (*B*) same sample disoriented thermally; cellulose acetate butyrate (*C*) drawn uniaxially and then disoriented thermally; cellulose triacetate, drawn, rolled, and annealed, (*D*) with beam perpendicular to plane of rolling; (*E*) with beam parallel to plane of rolling; (*F*) drawn, annealed, and rolled, with beam perpendicular to plane of rolling.

chain axes. In this plane they are not parallel to one another, nor are they highly ordered within the local confines of a crystallite. These conditions of structure specify particular properties within a given chemical composition, and must be accounted for in any interpretation of physical tests or in efforts to control physical properties.

PRESSING AFTER ELONGATION (UNIAXIAL AND BIAXIAL ORIENTATION). Molding as well as fiber spinning can produce uniaxial orientation, in which the main chain axes are approximately all parallel, in the fiber direction. A particular state of this orientation is shown in Figure 1*C* for a highly substituted cellulose acetate butyrate. Here, the fiber was drawn 500% (at approximately 170° C.) and annealed; within the crystallites the long chains can be assumed to occupy nicely fixed positions with respect to one another. However, in the uniaxial fiber these crystallites are randomly oriented around their own long axes.

The question is: What states would result if elements of the uniplanar orientation were introduced into the uniaxially oriented specimen? This can happen in injection molding, for example, when a melt is first extruded through a narrow circular opening, and then into a thin sheet, under high pressure. Ideally, the crystallites, parallel along the long-chain axes, would become oriented around these axes, and biaxial orientation would result. More than this actually occurs.

Figure 1*D* shows the result, with x-ray beam normal to rolled strip, of rolling at 25° C. the uniaxial fiber corresponding to *C*. The thickness of the final strip was less than one fifth that of the original fiber. A diagram taken parallel to the rolled sheet showed similar diffuseness. Figure 2*F* is a similar diagram taken perpendicular to the rolled strip made from cellulose triacetate under analogous conditions. Although the alteration in relative intensities (amounting in some cases to virtual disappearance) of the x-ray features shows that biaxial orientation has been caused, in addition, the original local order appears to have been strikingly disrupted. Poor resolution between equatorial spacings in Figures 1*D* and 2*F* suggests the familar process of lateral disordering around the main chain axes (*2*, *7*). Photoelastic fringes in these strips likewise indicated stored strains.

From this interpretation that biaxial orientation by "plastic" deformation increases the potential energy of the system by forcing chains from their equilibrium packing, it follows that annealing should reorder the system and sharpen the x-ray diagram. Figure 1*E* for the cellulose acetate butyrate and 2*D* and 2*E* for cellulose triacetate confirm this. Strikingly similar effects from mashing of raw cellulose have been noted and can be similarly interpreted (*18*). To what degree the evident re-resolution of some spacings and the half-breadth reductions of all are accompanied by reconversion of biaxial to uniaxial orientation on annealing will be discussed elsewhere, but it is not a large factor. However, in Figure 2*D*, with the beam normal to the rolled strip, and in 2*E*, with the beam parallel to it (but in all cases normal to the length of the strip), biaxial orientation evidently remains after reordering.

The disruption of local order by the mechanical stress bears a suggestive relation to the progressive weakening which accompanies the fatiguing of fibers and moldings. Quantitative estimation of improved ordering from this annealing is obtained either by intensity measurements on an appropriate, persistent feature, or by classification of missing features from comparison with the table of spacings given later.

Again, valid comparisons of physical properties could be made on these cellulose esters only if both orientation and local order were controlled. While proof of this assertion is outside the scope of this report, it appears in laboratory tests.

Table I. Interplanar Spacings[a] of Cellulose Esters Drawn, Rolled, and Annealed

Cellulose Triacetate				
	Intensity and Spacing, Å.			
Feature	0°		90°	
A_1	VS	10.43	VS	10.23
A_2	VS	8.58	VS	8.30
A_3	VS	6.53	VS	6.53
A_4	S	5.36	S/	5.24
A_5	M	4.68	S	4.68
A_6	M	4.15	W	4.11
A_7	M	3.73	M/	3.69
I_1	M	7.38	M	7.28
I_2			W	6.38
I_3	VS	4.92	VS	4.92
I_4	M/	4.21	M	4.15
I_5			W	3.85
I_6			VW	3.58
II_0	M	5.22	VS	5.18
II_1	M	4.73	M	4.71
II_2	M	4.43	W	4.37
II_3			M/	3.82
II_4			W	3.41
II_5			S	3.03
III_0	VS	3.30	S/	3.41
III_1			S	3.27

Cellulose Tributyrate				
	Intensity and Spacing, Å.			
Feature	0°		90°	
A_1	VS	12.55	VS	12.55
A_2	M	9.98	M	9.98
A_3			W	8.45
A_4	S	7.91	S	7.88
A_5	M	6.70	M	6.73
A_6	W	5.72	M	5.77
A_7	M	4.94	S	4.94
A_8	W	4.41	W	4.47
A_9	W	4.25	W	4.34
A_{10}	M	3.88	W	3.89
A_{11}	W	3.68	W	3.71
I_1	W	8.40	W	8.52
I_2	W	7.13	M	7.18
I_3	W	6.17	W	6.17
I_4	W	5.14	M	5.16
I_5	W	4.59	W	4.66
I_6	W	3.78	W	3.77
II_0			W	5.05
II_1	W	4.84		
II_2	M/	4.33	M	4.37
II_3	W	3.62	M	3.63
III_0	W	3.39		
III_1	W	3.37	W	3.27
III_2	W	3.17		

Cellulose Acetate Butyrate				
	Intensity and Spacing, Å.			
Feature	0°		90°	
A_1	VS	10.93	VS	11.00
A_2	VS	8.75	M	8.68
A_3	VS	6.83	S	6.80
A_4	S	5.55	M	5.58
A_5	S	4.87	W	4.92
A_6	M	4.32	W	4.34
A_7	M	3.83	W	3.86
A_8	W	3.46		
I_1	M	7.38	M	7.38
I_2	S	5.01	S	5.00
I_3	M	4.26	M	4.24
II_0	M	5.22	M	5.16
II_1	W	4.77		
II_2	M	4.45		
II_3	M	3.91		
II_4	W	3.41		
III_0	M/	3.39	W	3.38
III_1	S/	3.27		

[a] Position with x-ray beam perpendicular to plane of rolling is designated as 0°; parallel to plane, as 90°. Features are in order from center of diagram outward.

The marked change in fine structure when the sample of Figure 1*D* is converted to that of 1*E* by annealing for 3 hours at 100° C. (in the presence of small amounts of water vapor) has implications beyond even identification of the different states involved. It was found that the annealed strips had increased slightly in thickness; this effect, while conceivably the result of disorientation, actually reflected the indicated strain release.

Likewise, dimensional instability, unmolding, and warping are known to occur in moldings of cellulose derivatives, such as the acetate, on aging at high humidities. These are probably manifestations of such fine structure changes in the solid plastic.

LOCAL ORDERING AND DISORIENTATION

"Setting" accompanied by local ordering, which occurs in uniaxial fibers (*12*) as well as in the biaxial cases illustrated, can be carried out with no loss or perhaps with actual improvement in the over-all orientation. This is compatible with the significantly different activation energies expected for the rearrangement around the short axes in comparison with that around the long axes of the chains. Thus, by selection of annealing conditions favoring this difference, diagrams sharper and denoting higher order than those previously known are obtained. In addition to the examples of Figure 1*C* for cellulose acetate butyrate and 2*D* and 2*E* for cellulose triacetate, 2*A* illustrates the effect for a uniaxially oriented cellulose tributyrate fiber. In all of these cases present conditions lead to poor photographic reproductions, but high orientation and local order are plainly seen.

The upper limit for annealing by temperature (or swelling agent) is, however, lower for oriented than for unoriented polymers, because eventually the orientation of the long-chain axes is lost. This can easily happen in a compression molding kept hot through a long cycle. A significant point for the present topic is that such disorientation is, again, represented by a continuous series of states, unlike the sharp change on stretching rubber or polyisobutylene. Thus, within each state of orientation, described by the angular spread of the diffraction arcs, a whole range of degrees of local order, described by the appropriate line appearance and half breadth, may occur.

Such loss of high uniaxial orientation on further annealing is shown by the transformation of cellulose tributyrate pattern 2*A* to that of 2*B*. The ordered sample of 2*A* was annealed 30 minutes at 150° C. when dry (a few minutes otherwise), a condition leading to essentially complete reordering in an unoriented quenched sample. On heating, however, for 60 minutes more, a total of 90 minutes at 150° C., the slower process of disorientation asserted itself, and the long arcing of Figure 2*B* resulted.

This loss of orientation proceeds similarly, especially when moisture is present, for cellulose esters with residual hydroxyl groups, as shown by Figure 2*C* for cellulose acetate butyrate. Such disorientation is accompanied by shrinkage and other dimensional changes.

INFLUENCE OF ROLLING BEFORE DRAWING

One further example of the interconnection of orientation and local order concerns the influence on the final structure of the disordering caused by first rolling and then drawing the sample. Figure 1*F* is the diagram of cellulose acetate butyrate so treated. A strip from an isotropic film was first rolled to one fifth its initial thickness. This strip was then hot-drawn (but not actually melted) under annealing conditions which, without the preliminary rolling, would have given a sharp diagram of a uniaxial fiber resembling that in Figure 1*C*. However, it appears in 1*F* that the drawing did not pull the substituted cellulose chains out of the entangled and disorganized configurations of the initial strip, which had selective uniplanar orientation like that in 1*A* and 1*B*. The resolution of equatorial features in 1*F* is even less than in the disordered state described by 1*D*. Prolonged annealing gradually reorders the structure, but the rate suggests that numerous chain segments must rearrange.

This interesting superimposition of the effect of one kind of mechanical stress on another, carried out at a different temperature, extends the variety of structures which must be expected in characterizing cellulose esters.

ORDERED STATE AS REFERENCE STANDARD IN STRUCTURE

Once the various states of order and orientation in cellulose derivatives are recognized, there is the problem of specifying them quantitatively. This may be approached in various fashions, such as by measurements of the arcing in x-ray diagrams to determine the degree of alignment (orientation) (*37*), or by microphotometer tracings of selected features to determine the local order. There are many other techniques, such as density, dilatometry, thermal measurements, etc. However, the direct comparison of features in x-ray diagrams of a given sample with those in x-ray diagrams of the same composition in a "standard" or limiting state of both orientation and order may also be used conveniently.

Information to this end is given in Table I. Diagrams of rolled, highly annealed fibers were photographed at right angles

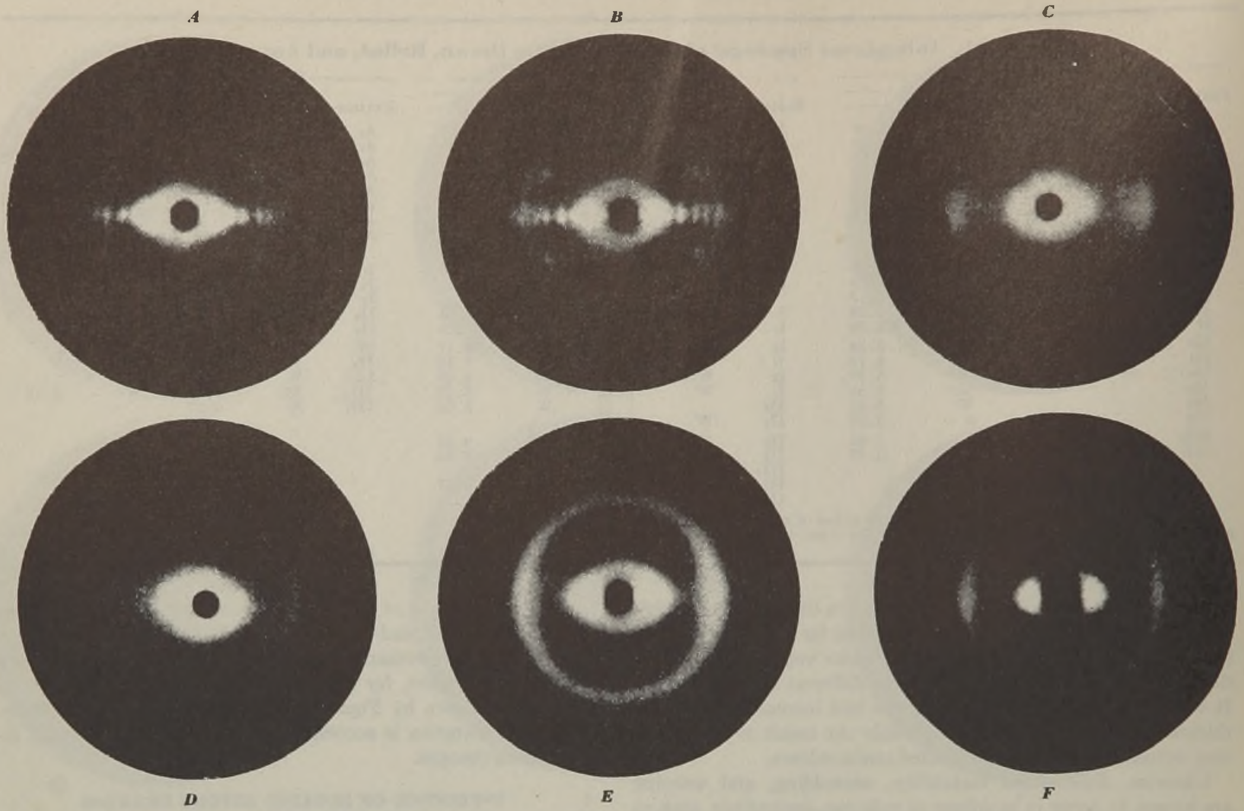

Figure 3. Effect of Substitution on X-Ray Diagrams of Uniaxial Fibers of Cellulose Acetate Butyrates to Show Chemical Limits on Local Order Attainable after Annealing

With molar proportions per glucose residue of *a* for acetyl, *b* for butyryl: (*A*) 2.2 *a*, 0.7 *b*; (*B*) 1.8 *a*, 1.2 *b*; (*C*) 1.9 *a*, 1.3 *b*; (*D*) 1.0 *a*, 1.5 *b*; (*E*) 1.2 *a*, 1.7 *b*; (*F*) 0.4 *a*, 2.0 *b*.

to the fiber axis, both normal and parallel to the plane of rolling. The interplanar spacings and relative intensities listed are for diagrams of maximum richness and sharpness. Actually, although the fibers were rolled, the less plastic compositions, such as cellulose triacetate, show only imperfect selective uniaxial orientation. Nevertheless, even where features are not actually absent in the 0° or 90° positions (of the beam with respect to the strip), their intensities differ sufficiently so that the effect of higher orientation is evident.

The features thus identified by characteristic spacings and intensities in Table I can easily be compared to the features actually observed in the poorly ordered diagrams of Figures 1 and 2, for example. Particular physical properties of a sample can then be related to the presence or absence of the A_6 spacing (4.33 Å.) in cellulose acetate butyrate, etc., as the case may be.

Detailed knowledge of how the individual chain configurations change from one state to another would be highly desirable. Unfortunately, the exact structure of such high polymers is almost never known because of inadequate or ambiguous data. Patterson (*32*) recently discussed the limitations of such structure analysis, often overlooked. Even with fairly rich data, factors treated by Patterson must be considered before a "crystal" structure, or molecular structure deduced from it, can be derived. Nevertheless, spacings such as those in Table I often represent well the interchain separations and arrangements. The equatorial spacings, affected according to certain general principles of substitution (*4*, *5*, *7*) and chain order (*2*, *3*, *7*) often give reasonable indications of the very intermolecular spacings which determine physical properties.

LOCAL ORDER AND DIFFERENT "FORMS". Apparent variations in these equatorial spacings, accompanied always, it is important to note, by changes in sharpness of the spots, have led to the vast literature (*38*) on different forms of cellulose derivatives. Present knowledge makes it probable that the numerous "forms" of cellulose esters, ethers, etc., reported really represent different states of local order as discussed above. Thus they are not actual polymorphic forms stable only over certain temperature ranges or conditions of preparation.

Some evidence suggests that native and hydrate or mercerized (*1*, *33*) cellulose are not separately stable forms, but they represent far more distinct structures than do the derivatives. It was, however, early indicated that the chain packing was rearranged, in the hydrate form, into positions of closer, more stable, interaction (*1*). It is possible that the deposition of native cellulose, like the deposition of cellulose derivatives from certain solvents (*7*), leads to a state of higher free energy than the hydrate structure. Suitable swelling agents would thus allow conversion of native to the hydrate. With this idea in mind, it was found that some biological conditions apparently could lead to the more stable hydrate form in the first place (*36*). However, by this mechanism different mercerizing treatments would be expected to cause slightly different ordering in the final hydrate form. There is, again, some evidence for this.

Consistent with these ideas is the recent discovery that suitably vigorous treatment apparently can convert hydrate cellulose back into native (*22*, *28*). The methods used correspond to strong disordering, and the treated cellulose may then have been recovered in this less ordered state.

Similar circumstances appear in all of the lengthy descriptions of different "forms" of the derivatives. In these x-ray patterns, however, relatively sharp differences like those between native and hydrate cellulose are usually lacking. It is striking that emphasis is on the differences in sharpness and intensity of the diffraction spots rather than in their actual arrangement, in an

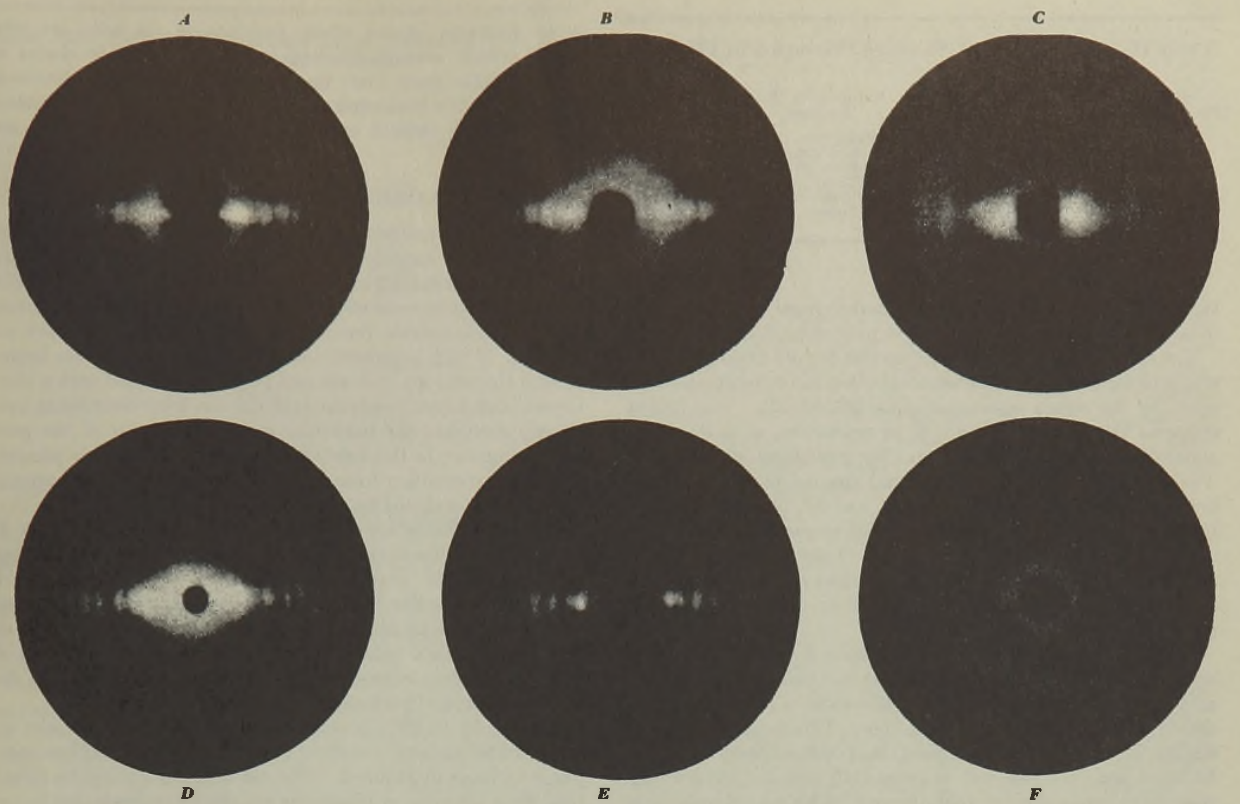

Figure 4. Disordering of Cellulose Acetate Butyrate, Uniaxially Oriented, by Plasticizers

(*A*) 15% dimethyl phthalate by weight; (*B*) 20% dimethyl phthalate; (*C*) 30% dimethyl phthalate; (*D*) 30% dibutyl sebacate; (*E*) mixture with incompatible "ester oil"; (*F*) 15% dimethyl phthalate with unoriented sample, quenched.

account of methylcellulose I and II (*44*). Yet two distinct forms were described. They might rather be regarded as two from a great number of possible states of order around the chain axes, as denoted in Figures 1 and 2 and elsewhere (*2*, *7*, *12*). Similarly, with cellulose triacetate I and II (*19*) "form I" has the larger intense equatorial spacings (>10.35 Å.) characteristic of the states whose chains are laterally disordered (*7*, Table I). This explanation that cellulose triacetate I is a metastable, locally disordered state also agrees with the extensive observations that agents such as cyclohexanone increase the lateral spacings during swelling of form I. For this disordered form already has elements of liquid structure, which can be continuously changed by swelling or other admixture since only averaged interplanar spacings are involved. On the other hand, the form of maximum order, II, could not show such reversible swelling changes and remain as II, since in it the chains are precisely arranged; if swelling were accomplished, the fixed structure would be disrupted.

This interpretation of forms I and II is, further, compatible with studies on acetylation and deacetylation at various temperatures, and on the nature of films formed from solvents at different temperatures (*21*). While this work realized the effect of solvents on the crystallite size in the resulting films (*39*), there was no consideration of disorder within the crystallites themselves. Thus, rather than the simple interpretation now proposed to account for the different forms, numerous molecular complexes or addition compounds were suggested to form between cellulose esters (including the nitrate) and the given solvents (*45*) or polymer degradation materials present (*11*). Such assumptions of complex formation, or of other special structures, seem unnecessary to account for the variety of x-ray patterns and associated physical effects of forms I, II, etc.

CHAIN SUBSTITUTION AND DISORDERING

The principles in this report emphasize that the physical properties observed for a given cellulose derivative describe only that derivative in a particular, specified state of order and orientation. It is realized that different highest or ultimate states of order are accessible to different chemical compositions. Thus, unless composition is carefully controlled, indications of local disorder, such as in an x-ray pattern, may be wholly attributed to thermal history, solvent treatment, etc., of the polymer when they might actually mean a permanent local disorder corresponding to incomplete substitution, etc.

From this point of view, Figure 3 is presented to show typical effects, on ultimate order, of the degree of substitution in a mixed ester, cellulose acetate butyrate. The samples are designated in Table II according to their position in Figure 3. Table II also shows the average molar substitution of each polymer (*13*) and its distribution among acetyl and butyryl residues (*13*), as well as A_1 x-ray spacings strongly influenced by average substitution.

It has long been known that degree of substitution causes striking changes in x-ray patterns of cellulose derivatives (*38*); Trillat (*42*) reported that 12.95% combined N in cellulose nitrate gave a crystalline pattern while 12.0% N corresponded to an amorphous state. However, there had been no assurance that the effects were wholly from chemical composition and not complicated by quenching, solvent action, etc. This is especially possible when there is incomplete substitution, since the intermediate states of order often appear to be truly stable (*7*). Hence, all of the patterns of Figure 3 were obtained from samples highly annealed or otherwise treated to represent the highest local order attainable for the given chemical composition. Uniaxially oriented fibers, fiber axis vertical, were used.

As expected, only the esters essentially completely substituted yield ordered diagrams. But even so, nearly complete substitu-

Table II. Description of Samples Presented in Figure 3

Sample	Total Substn., Moles	Molar Substn.		Nature of X-Ray Diagram	X-Ray Side Spacings A_1, in Å.
		Acetyl	Butyryl		
A	2.9_5	2.2	0.7	Ordered	11.10
B	2.9_8	1.8	1.2	Sharp, ordered	11.41
C	2.2	0.9	1.3	Diffuse	13.3
D	2.5	1.0	1.5	Diffuse	12.4
E	2.8_5	1.2	1.7	Diffuse	~13.4
F	2.4	0.4	2.0	Diffuse	13.8

tion such as that for sample 3E, containing roughly equal amounts of acetyl and butyryl residues, leaves permanent disorder.

The last column of Table II illustrates the old finding that increase in the length of the substituent chain increases the spacings given by the strong equatorial spots (*20*, *37*, *43*). But it also supports the point made earlier in connection with the large equatorial spacings that arise from disordered forms of the esters. Thus, while the strongest equatorial spacing for cellulose tributyrate is 12.6 Å., samples 3*C*, 3*E*, and 3*F*, all below the tributyrate in substitution, have somewhat larger spacings. These equatorial features do not show well in Figure 3 because of scattering near the primary beam. The actual measurements were made on films exposed for a shorter time. In these, moderate precision could be attained.

Similarly, among the disordered samples 3*C*, 3*D*, 3*E*, and 3*F*, only sample 3*D*, with its smaller equatorial value, shows reasonably good uniaxial orientation. However, all samples were drawn under closely similar conditions. This suggests the possibility, also implied by other data, that ordered crystallites can be more perfectly (but not more easily!) oriented by drawing than those containing internal disorder. This may simply be a consequence of the fact that more ordered systems require more tensile stress to be oriented (*12*) and have a lower breaking elongation. Thus, perhaps such systems actually impose higher inner restraints on the long chains. The drawing conditions used would not show this difference in tensile stress, since "closely similar" conditions are taken to mean drawing to a constant elongation at a given rate and temperature (temperature being adjusted for each composition).

Evidently local disordering because of chemical composition, shown in Figure 3, resembles in many ways the disordering from quenching, solvents, and mechanical working. However, since it cannot be annealed out, unlike the other cases, it would be expected to affect still other intrinsic properties such as melting point. This seems to appear in the melting point behavior of the systems (*24*) as a cause of the hook-back of the curves relating melting point to composition. These go toward the low-melting-component side as the total substitution is increased. For example, the butyryl content of a cellulose acetate butyrate can actually be increased without the melting point of the mixed ester being lowered, if the total substitution is likewise suitably increased so that more ordered structures are formed. Table II and Figure 3 illustrate how critically the degree of crystal-like structure depends on total substitution, but it may be supposed that "melting point" itself changes more gradually than the x-ray patterns. Hence, the melting point curves inflect gradually over a range of compositions.

Finally, even though high substitution in the mixed esters yields, according to the x-ray diagrams, chains whose positions in the solid are relatively orderly around the long axes, the acyl side chains of mixed lengths must limit the ultimate local order. Details of this more subtle limitation will appear only when the positions of atoms with respect to those in neighboring chains are determined.

PLASTICIZERS AND CHAIN ORDER

Cellulose derivatives are presumably soluble in "compatible" plasticizers. A large (often predominant) factor in the dissolution of linear polymers in organic solvents is the entropy of solution. Its large increase often offsets unfavorable heats of solution and causes favorable free-energy change (*29*); later work on solutions of high polymers is based on these ideas. The beginning of this entropy increase, as a polymer is diluted with a plasticizer, is expected to appear just like the local disordering previously discussed for particular metastable states of the pure solid. Further, in this case as long as the plasticizer is present, the disorder resulting from indefinite positions of chains around their long axes should be stable.

These conditions are indicated by the diagrams of Figure 4. They are from plasticized compositions of the highly substituted cellulose acetate butyrate described under "Preparation of Materials". Similar results were found whether the compositions were made by mixing in the plasticizer on hot mill rolls or in solution with a volatile solvent such as chloroform. All of the fiber patterns represent annealed states, confirming that the plasticizer causes "permanent" disorder in sample 4*C*, etc.

Apparently 15–20% plasticizer (4*A* and 4*B*) still permits an ordered fiber pattern, but the individual features are diffuse compared to those in Figure 2. The old argument might be raised that these amounts of plasticizer are chiefly concentrated in the amorphous regions. The marked change in relative intensity of

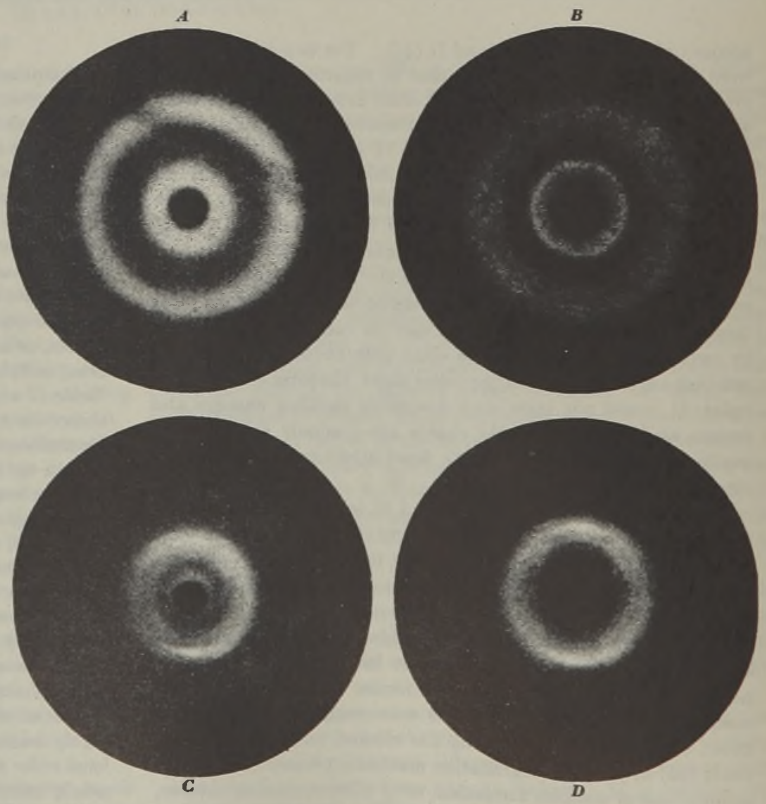

Figure 5. X-Ray Diagrams of Starch Triesters

(*A*) tapioca starch triacetate, unoriented; (*B*) cornstarch triacetate, drawn uniaxially; (*C*) tapioca starch tributyrate, unoriented; (*D*) potato starch tripropionate, drawn

Table III. Principal Spacings from Oriented and Unoriented Starch Triesters[a]

Feature	Unoriented Starch Triacetate, d, Å.	Unoriented Starch Tripropionate, d, Å.		Unoriented Starch Tributyrate, d, Å.
R_1	12.9–13.9[b]	VS	12.6 $S^{/}$	13.4 $S^{/}$
R_2	9.4– 9.8	VS	....	....
R_3	6.7	W	....	....
R_4	5.4– 5.5	W	....	....
R_5	4.2	W	4.4 $M^{/}$	4.4 $M^{/}$
R_6	3.4	W	....	....

Oriented Part of Tripropionate

	d, Å.
A_1VS	9.45
A_2M	5.14

	Fiber Period, Å.
I_1M	17.5
I_2M	16.7
II_1M	17.5

Oriented Part of Starch Triacetate

		d, Å.
A_1VS		9.38
A_2M		5.14 (arc)
A_3W		4.49
R_1W		14.73
R_2S		11.93
R_3W/		4.47
R_4M		4.15
	Fiber Period, Å.	
I_1M	16.9	11.83
I_2W	16.3	8.35
II_1M	17.4	6.35
II_2W	17.7	5.26
II_3W	16.5	4.54
V_1VW	(17.8)	(3.69)

[a] Superscript / means fuzzy feature.

[b] Apparent variation over range of sources of starch; potato and tapioca, low; corn, wheat, and rice, high. May be effect of different sample preparations on chain kinking.

some of the layer line features in progressing from 4*A* to 4*B* indicates, on the contrary, that the plasticizer is gradually disordering the whole structure.

When 30% dimethyl phthalate is present, as in Figure 4*C*, poor orientation and order (both reminiscent of cases in Figure 3) result. Nevertheless, the equatorial spacings remaining are only slightly larger than those in Table I for the ordered polymer; thus $A_3 = 6.95$, $A_4 = 5.58$. The other longer equatorial spacings are diffused.

The disordering is less for 30% dibutyl sebacate, as shown in Figure 4*D* by resolution of longer equatorial spacings and retention of layer line spots. While 30% dibutyl sebacate corresponds to 1.28 times, or about a quarter more than the volume of 30% dimethyl phthalate, the significant point is probably the molar proportions. Plasticizing is apparently best done by weakening the forces within the layers of dipoles throughout a polar polymer (*3, 4*). The number of plasticizer molecules which can associate with specific groups (*14, 15*) in the polymer would thus determine the disordering (softening) effect of the plasticizer. There are only 0.62 times as many dibutyl sebacate molecules in sample 4*D* as dimethyl phthalate molecules in 4*C*. This seems to account for the difference in the local order and is again a factor which appears in evaluation of physical properties. In this connection, although the cellulose acetate butyrate used in Figure 4 had a relatively high acetyl content, no question of incompatability with dibutyl sebacate up to 30% arose to complicate the interpretation.

However, polymer-plasticizer mixtures where two phases exist can also be studied by x-ray diagrams. It is desirable to have background information on the fiber pattern of the most ordered form of the given polymer composition and on the approximate changes which occur when a compatible plasticizer is taken up by the structure. Then, a fiber may be drawn from the given composition of cellulose ester and plasticizer whose compatibility is being investigated. When the polymer is wholly or partially insoluble in the plasticizer, diagrams resembling those in Figure 4*E* result. The typical liquid scattering of the undispersed plasticizer appears as halos superposed on the fiber diagram. The high resolution of equatorial spots in this diagram indicates little penetration of the structure by the plasticizer, which apparently persists as a separate phase. Detection of this phase is naturally limited if the pattern of the cellulose derivative studied is too diffuse.

These considerations of the effect of plasticizers on interchain (local) order, so far illustrated with fiber patterns, apply equally well to unoriented samples. Another factor can also be shown here. That is, with limited amounts of plasticizer, the compositions are locally disordered further by quenching, just as with the unplasticized polymers. Although with plasticizer present, quenched states are annealed out relatively rapidly even at room temperature, the changes during this annealing can still complicate tests on physical properties made shortly after molding. Figure 4*F* shows the pattern for the same cellulose acetate butyrate composition, with 15% dimethyl phthalate, as in the fiber diagram of 4*A*. However, the unoriented sample of 4*F* was also quenched. The diffuse rings show lateral disorder of the chains (*2, 7*) in addition to that introduced by the plasticizer. If the sample of 4*F* is suitably annealed, a Debye-Scherrer pattern results, of sharpness comparable to the features in 4*A* (an annealed pattern). This factor of metastable local disorder with plasticizers may be generally anticipated in addition to (stable) disordering caused by chemical composition (*15*). Also, a metastable disordering from the presence of small residual amounts of volatile solvent probably accounted for changes noted on aging of thin films of celluose esters used for electron diffraction (*26, 41*).

STARCH TRIESTERS

Mixtures of synthetic linear polymers whose respective chains differed slightly (only in the spacing of polar linkages) were found to order and orient in separate phases (*3*). The solid containing this mixture generally obeyed, however, the principles discussed above. Similarly, the behavior of cellulose and its derivatives such as the triesters appears also in many properties of analogous starch systems. But the heterogeneity and limited thermoplasticity and solubility of starch, occasioned by seemingly different structures of branched (amylopectin) and linear (amylose) components (*8, 27*) add new variables in the over-all structure of the solid.

Figure 5 shows typical x-ray diagrams of whole starch triesters. Significant differences from the corresponding cellulose triesters are superficially apparent. These and other starch esters studied were kindly prepared by J. W. Mullen, II, under carefully controlled conditions which minimize degradation (*31*). This is a critical point. Patterns in 5, for tapioca starch triacetate (5*A*) and tapioca starch tributyrate (5*C*) are from annealed, unoriented, unplasticized sections prepared by our usual techniques of mill massing or molding. The tributyrate reveals only a moderately ordered diagram. The longer acyl residues encourage some, but relatively much less, disorder in chain packing in cellulose derivatives. However, the further question is: How does the mixture, of presumably linear and branched species, affect the structure and limit the local order? Within a given chemical composition, chain branching in synthetic polymers inhibits close packing and local ordering of the chains according to unpublished studies made in these laboratories.

Fibers made from the triacetate of a separated amylose fraction yielded a moderately sharp fiber diagram, said to be the first fiber pattern reported for starch or its derivatives (*47*). Further, on the basis of studies on other preparations from the amylose fraction (*35*), the x-ray pattern of this part was suggested to represent the crystalline features exhibited by whole starch (*34*). However this may be, patterns 5*A* and 5*C* imply that the larger butyryl groups, compared to acetyl, disturb the interchain order much more in starch than in cellulose. Presumably both amylose and amylopectin portions are affected, or at least there is no evidence that one is affected to the exclusion of the other. If the amylose is the only ordered phase, then it is particularly disturbed; and by substitution with butyryl, its x-ray scattering is made to coincide with that of the amylopectin tributyrate. The starch chain sections may be partly crumpled (*27, 34*) and thus readily changed in configuration by substitution of the larger acyl residues which interact along a given chain (*4*). These effects appear in simpler carbon chains (*6*). So, in these systems sensitivity to chemical disordering may be anticipated, and may appear in one or both phases. Quenching, or other physical disordering, will appear likewise, although the slight thermoplasticity of the whole-starch derivative restricts the range of states of order attainable.

In addition to these factors in local order in starch and its derivatives, their structural response to orienting forces is less clear-cut than that of the cellulose derivatives discussed before. Figure 5*B* is a pattern obtained from a filament of cornstarch triacetate (*31*) prepared by extrusion of the hot "melt" (not truly thermoplastic) through a fine nozzle under high pressure. Part of the diagram exhibits relatively high orientation and local order; the rest shows a little local order without noticeable orientation. That is, apparently in one phase, chains have been well aligned (uniaxially) by extrusion; this would presumably be the amylose triacetate. Similar effects appear in Figure 5*D* for potato starch tripropionate.

Thus, in these systems, in addition to the range of coexisting states of order and orientation shown for cellulose derivatives, a given sample may apparently possess high orientation of one fraction and a more random arrangement of the ordered regions of the other, presumably the branched amylopectin triester. This suggests that molecules or chain sections of these two fractions do not pack together in the same ordered regions, or "crystallites", in the whole-starch triacetate. Sufficiently highly branched or netted molecules would not be miscible with a linear species such as amylose is thought to be.

Diagrams such as those in Figure 5*B* have permitted identification of some of the spacings observed in Debye-Scherrer diagrams from the whole-starch triesters. These are listed as lateral (A's), or as some derivative of the fiber period, I, along the chains, in Table III.

The best values of about 17.5 Å. for the fiber period are somewhat below the value of 18.3 Å. previously noted (*47*) for a different sort of amylose triacetate which had been separated from the whole starch. The similarity in strong A_1 spacings of both starch triacetate and tripropionate is interesting. The chain configuration is clearly different from that in cellulose esters. In the last column of Table III the features denoted by the I_1 layer lines and the R_2 ring are distinct, although the angular separation is very slight. The ring in this and other instances may come from the branched structure which has some spacings very close to those of the oriented phase.

The diagrams in Figure 5 represent systems in which the native starch was highly dispersed during esterification (*31*) and then reagglomerated. The distribution of fractions in it is presumably influenced by this process. However, applications of structural principles found for cellulose derivatives have many interesting implications here.

SUMMARY

1. X-ray diffraction studies on cellulose triacetate, tributyrate, and mixed acetate butyrates portray local chain order as well as over-all orientation resulting from mechanical operations such as molding, extrusion, drawing, and rolling. Such structural characterization is necessary in interpreting the results of tests of physical properties.
2. Varying degrees of order around the long-chain axes of solid cellulose derivatives, previously shown for unoriented samples, have been found in oriented fibers and sheets.
3. In addition, operations similar to those which occur in molding may cause degrees of uniplanar, selective uniplanar, uniaxial, or biaxial orientation in these polymers.
4. Strains stored in cellulose esters by cold working, such as by rolling sheets, are discernible as local disorder of the chains. The mechanical deformation appears to be accompanied by rotational motion of chain sections and leaves some degree of disorganization around the long axes. This can subsequently be removed by annealing. Such reordering at ordinary temperatures may account for the slow aging often observed in physical testing.
5. Effects of one kind of working, such as rolling, on a subsequent operation, say drawing, are detectable in the x-ray structure of the final sample. For instance, under comparable conditions, a cellulose ester, first cold-rolled and then drawn, is less ordered than if drawn without previous rolling.
6. Fiber patterns from polymers of known orientation and maximum order (highly annealed) provide standards for comparison with x-ray patterns obtained for samples of unknown characteristics. Measurements of these ordered patterns have been tabulated for cellulose triacetate, an acetate butyrate, and tributyrate.
7. Cellulose ester x-ray diagrams, which have been supposed in the literature to represent different polymorphic forms, such as cellulose triacetate I, II, etc., may simply reflect different degrees of metastable local order. Affirmatively, the larger spacings from the A_1 spots found in form I compared to form II are also typical of polymers quenched or otherwise disordered.
8. Degrees of partial or mixed substitution can cause permanent, as contrasted to metastable, local disorder. Hence, these compositional factors must evidently be carefully controlled, along with molding conditions (cooling, etc.) to yield consistently similar structures in the final plastic.
9. Plasticizer also disorders the polymer molecules progressively as its amount is increased. Comparison of the effects of dimethyl phthalate and dibutyl sebacate supports ideas that the number rather than total volume of plasticizer molecules chiefly determines the disorganization of dipole layers. Heat of solution must likewise be considered, however.

ACKNOWLEDGMENT

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IMPACT TESTING of PLASTICS

Relation to Structure and Composition

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Several factors play a part in rapid mechanical deformations, and they may be studied by the use of mechanical models whose mathematical characteristics simulate the behavior of real materials. A correspondence may be drawn between the model elements and structural features such as primary and secondary bonds. The question of materials being characterized by a continuous range of bonds differing in time constants is examined. It is shown how the concept of bond breakage and re-formation as a function of thermal energy fluctuations can explain the known inverse rôles of velocity and temperature in many mechanical phenomena. The value of a dispersion of bond properties in making materials resistant to impact fracture is pointed out. The effect of notches or cracks upon the stress distribution is illustrated, and it is shown how these play a part in determining the relative behavior of different materials. The propagation of shock waves in the material subjected to an impact blow is discussed, together with the question of their dissipation by a dispersion of certain bond qualities. It is pointed out how such well-known factors of impact resistance as plasticizer and moisture content, temperature, molding conditions, etc., enter into the phenomena of fracture propagation, bond dispersion, stress concentration, and shock wave dissipation. A number of workers, particularly in the metals industry, have been developing in recent years experimental methods for obtaining complete stress-strain curves during a short time of impact loading. These methods are illustrated in this article, and are compared for their ability to yield information about the general stress-strain-time-temperature behavior of a material.

IN THE execution of an impact test, a number of more or less independent factors are called into play, and their effects are integrated into a complex action. This complex of separate effects does not consist of the same relative amounts of the component factors for all impact tests. Their relative amounts vary according to the type of material, dimensions of the test piece, previous molding history of the test piece, etc.; since some of these factors are mutually opposing, it is possible to have peculiar inversions of what should be a logical sequence of impact strengths.

Such factors include stress distributions at notches, cracks, or discontinuities, as well as shock waves and their reflections. They include temperature and impact velocity as these, in turn, affect the stress-strain relation. We shall see further that an important consideration is the manner in which a fracture is propagated through the specimen. This is linked to the hysteresis or damping properties of the material.

When we are able to study and measure such factors separately, we can learn how to blend the right amount of each into a single result which will have good correlation with the impact behavior of the material in actual service. While we may, by the study of mechanics, treat each of these as a separate factor, each in turn is due to underlying molecular and polymer chain properties. Thus, the more we are able to relate such things as a modulus, or damping factor, to molecular structure, the better will we be able as synthetic chemists to improve the material.

MECHANICAL PROPERTIES OF HIGH POLYMERS

Attempts to explain and predict the complex behavior of organic polymers, particularly with regard to the influence of time and temperature, have been made for the past hundred years. Even before the structural details of a high polymer were known, it was found possible to set up a mechanical model of springs and viscous pistons whose behavior would simulate that of many plastic substances. A spring and piston in series is referred to as a Maxwell body, and obeys a differential equation first proposed by him. It was not necessary to attach structural significance to the springs and pistons; they merely served to illustrate the function of the mathematical expressions which, when properly combined, gave the correct stress-strain-time curve (*10*). Figure 1 shows some models, with the corresponding graph of their mechanical behavior when subjected to slowly increasing forces and to impact blows. When the viscosity is high, the total extension is almost entirely due to the spring, and rupture occurs at the limiting extension of the spring. For a Maxwell body with short relaxation time, a considerable plastic deformation can occur, with a resultant greater energy or work absorption. When the time rate of application of the force is increased to correspond to impact blows, then less plastic deformation occurs and less energy to rupture is required.

Figure 2 shows the type of curve obtained when the two Maxwell bodies are connected in parallel. The left-hand diagram shows the curve shape for normal temperatures; at slow loading rates there is considerable plastic deformation. At impact rates sufficient time is not available for even the body of low viscosity to extend plastically. The same result is obtained also by decreasing the temperature, as shown in the diagram on the right. In this case the viscosity is increased so that even at moderate rates of loading the body is brittle. The extent to which the temperature must be lowered to achieve brittleness is a measure of the fluidity of the dashpots and hence a measure of the energy which is taken up in an impact blow at normal temperatures.

Figure 3 shows a more general mechanical analogy; there is a spring of small range in series with the whole which represents the small elastic displacement found in all solids. Next, we note two springs and two Maxwell bodies in parallel. Spring S_1 represents an elastic mechanism of considerable extensibility

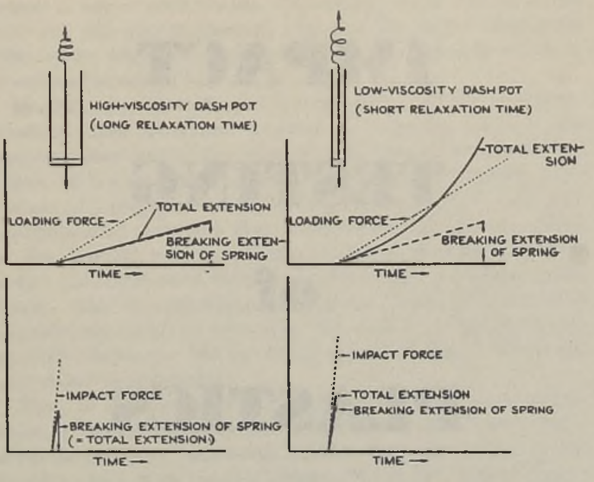


Figure 1. Models of Maxwell Bodies with Graphs of Mechanical Behavior

but of small force constant, which we may identify with the skeleton network of chains connected to one another by primary cross links or by crystallization into two or more crystallites.

The two Maxwell bodies represent the distribution which one may expect from a number of secondary bonds of different type and strength. Spring S_4 represents the elastic force which appears in rubber and some other polymers, owing to the tendency of chains to seek the most disordered and kinked state. Higher temperatures lead to an increase of this retraction force. The recognition of this type of mechanism is due to Kuhn, Mark, and others. The table of Figure 3 contains some brittle temperatures and elastic incidence temperatures, and indicates how they may be pictured in terms of the mechanical body.

In the mechanical model proposed by Maxwell, the characterizing constant of the body is the relaxation time. This quantity is the time necessary for the retractive force exerted by the Maxwell body when held at a constant extension to decay to $1/e$ of its initial stress value. An alternative method, used by Alexandrov and Lazurkin (*2*) and by Tuckett (*23*), is to consider the elemental body as a spring and piston in parallel, rather than the series arrangement of Maxwell, and to characterize this elemental body by an "orientation time" which is the time required for the body to attain $1/e$ of its final deformation, under a constant force. This conception of a relaxation time fits in well with the study of dielectric relaxation times made by Fuoss (*11*).

Thus, one may attack the problem by searching for the forces which the various primary and secondary bonds contribute, when deformed, or one may add up the deformations which are obtained under known forces applied to the separate bonds. As illustrative of the results obtained, we may give the expression for the total deformation of a body as:

$$D = \frac{S}{G_{OE}} + \frac{S}{G_{HE}}(1 - e^{-t/\tau}) + \frac{St}{\eta}$$

where S = applied stress
G_{OE} = modulus associated with the small elastic displacement
G_{HE} = modulus associated with long-range elastic causes
t = time
τ, η = constants

At low temperatures τ and η are large. Thus, at low temperatures or short loading times (impacts), the deformation is given by the first term only. The last term represents the continuous plastic flow of a body which lacks a network or skeleton structure that will end the deformation.

The form of the equation expressing the mechanical properties of a material, when a whole spectrum or distribution of values of relaxation times is present, becomes considerably more complex and difficult to handle. Discussions are given by a number of writers (*3*).

FLOW PROCESSES AND ACTIVATION ENERGIES

In the present-day literature on the mechanical properties of high polymers, time effects are usually ascribed to the presence of two different types of bonds, called "primary" and "secondary". The primary bonds form a sort of skeleton which, in the case of cellulosic derivatives, may be identified with chains crystallized into two or more crystallites. In the case of thermosetting phenolic plastics, these primary bonds are chemical cross links.

The secondary bonds are considered to arise from van der Waals, hydrogen-bridging, dipole, or London dispersion bonds, and are continually breaking and re-forming, at a rate dependent upon the violence of kinetic thermal motions and on the energy of activation, U, of the bond. According to whether we consider U the same for all bonds, or whether there is a whole range of values $U_1 \ldots . U_n$ for different bonds, we have Maxwell's picture of a material, or that proposed by Wiechert (*27*) and later treated by others, of a whole spectrum of relaxation times.

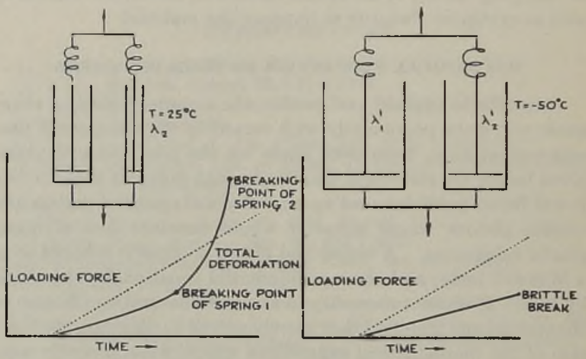


Figure 2. Curves Obtained When Two Maxwell Bodies Are Connected in Parallel

It has remained for later authors (*9*) to formulate these concepts more exactly in terms of an activation energy which must be imparted to a pair of molecule segments or atoms or groups before they can flow past one another. A generalized picture of their work may be summarized as follows: The rate at which cohesive flow of chain segments past one another can take place is given by:

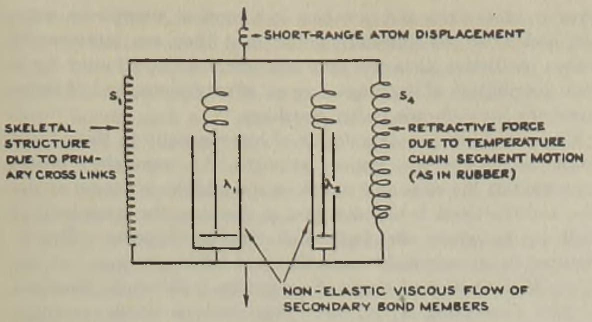
$$R = Ce^{-\frac{U}{kT}}$$

and U is the energy of activation necessary to overcome the attractive energies of the segments or chains which move past one another. With no force applied to the body, the probability is equal for a viscous flow in any direction; thus, there is no resultant observable strain. But if a force is applied, then the rate of "flow mechanism activation" is greater in one direction than another. For if the size of the potential energy barrier which keeps the units in their original places is U, an applied force lowers this barrier in the forward direction of the force and increases the barrier in the opposite direction. We can assume this change of U to be proportional to the stress. The new energies are then $U - AF$, $U + AF$, and the corresponding flow rates are:

$$R_{\text{forward}} = Ce^{-\frac{U-AF}{kT}}$$

$$R_{\text{opposite}} = Ce^{-\frac{U+AF}{kT}}$$

$$\text{Net rate of cohesive flow} = Ce^{-\frac{U}{kT}}\left[e^{\frac{AF}{kT}} - e^{-\frac{AF}{kT}}\right]$$



POLYMER	TEMPERATURE AT WHICH LONG RANGE ELASTICITY BECOMES NOTICEABLE [S_4 LARGE, λ_1, λ_2 SMALL]
RUBBER	−50° C.
VINYON (POLYVINYL CHLORIDE-ACETATE)	+70° C.
POLYSTYRENE	+80° C.
POLYSTYRENE + CROSS LINKER	MUCH HIGHER
POLYMETHYL METHACRYLATE	+90° C.

Figure 3. General Mechanical Analogy

Thus, the inverse of this rate for unit stress gives an orientation or relaxation time characteristic of the material,

$$\tau = C_1 e^{\frac{U}{kT}}\left[\frac{kT}{A} - \frac{A}{6kT} + \frac{1}{51}\frac{A^3}{k^3T^3}\right](A < kT)$$

From this discussion, we see that a material is characterized by a relaxation time or times in which temperature plays an important part. The major influence of temperature appears in the exponential term $e^{U/kT}$, and hence low temperatures produce long relaxation times.

Recalling the formulas which represent the force-deformation-time characteristics of the various spring and piston models, we note that a deformation was accounted for by expressions containing terms t/τ, in which t is the time of duration of the applied force or may represent the time allowed for deformation. Action time and relaxation time always appear as a ratio, and since the latter contains the factor $e^{U/kT}$, in any mechanical process, action time and temperature are linked together in a form of approximately $te^{-(1/T)}$.

We can formulate the conditions for brittle fracture as follows: Denote by L the average distance traversed by two structural units which part from each other and flow to bond again with the next neighbor unit. The average time required for this process is the time required for the bond to acquire more than its activation energy, U, for a given force applied; this time is approximately proportional to $e^{U/kT}$. The "limiting cohesive flow velocity" is then $CLe^{-(U/kT)}$, and this is a measure of the limiting or critical velocity which the hammer or falling weight may have without producing a brittle fracture. As discussed before, a more exact expression follows from making the value of U dependent on stress.

We have, therefore, a theoretical basis for what has been so long known experimentally, that an increase in velocity or a decrease in temperature acts in the same direction—lessening flow processes and causing brittleness. In fact, the use of such a relation was proposed by Zener and Hollomon (*28*) as a convenient way of measuring the impact properties of steel without going to high velocities, by conducting slow rate tests at low temperatures. Data on steels are presented which show good agreement.

This interrelation of temperature and velocity is the basis for two impact methods of testing in use. One is to measure that low temperature at which brittleness appears, using a slow deformation rate. The other is to hold to room temperature and to find that critical speed of impact at which brittleness appears.

A thorough study of the relation of the temperatures and velocities required to produce brittleness in soft steel has been made by Vitman and Stepanov (*25*).

The critical velocity, V_b, and the related critical temperature, T_b, to produce brittle fracture were found to be related by the formula

$$V_b = Ce^{-\frac{C_2}{T_b}}$$

which affords a good experimental basis for the theoretical picture.

Even before the work of Vitman and Stepanov, Schwinning and Matthaes (*21*) found, for notched steel, a similar relation for speeds of 10^{-5} to 3 meters per second.

The interlocking connection between velocity and temperature, for the production of a given physical state, has also been discussed by Nadai and Manjoine (*20*). These authors show that the point of maximum stress which steel will support in tension depends on certain critical values of both the strain rate and temperature, and that an increase in strain rate or a decrease in temperature from the critical values for maximum stress causes a drop in this property.

The fact that in impact phenomena an adiabatic rather than an isothermal process is present has already been recognized by several writers. Since the steady temperature just prior to the test is much more readily determined than the actual momentary temperature, and since the former is generally used in establishing a relation between velocity and temperature, it is advisable to know what error might be introduced. Nadai and Manjoine, by the use of a thermocouple and string galvanometer, found that the maximum temperature rise in a steel test piece broken in 0.002 second was 50° C.

Haward (*13*) examined this question with reference to the rapid deformation of celluloid and cellulose acetate, and concluded that the temperature difference between isothermal and adiabatic processes does not play a large part in causing the differences observed in the fast and slow deformations of these materials. This is apparent from the following data and calculations of Haward:

Material	Sp. Gr.	Sp. Heat	Max. Extension, %	Max. Possible Temp. Rise, ° C.
Celluloid	1.40	0.34	30	10
Cellulose acetate	1.28	0.41	50	4.7

Impact velocity is an independent variable with an effect, per se, on the type of deformation in addition to possible secondary effects of induced temperature changes.

Two German metallurgists, studying impact measurement twenty years ago, formulated some ideas on brittleness and impact breaking which are remarkable for the manner in which they foreshadow the present line of thought. They did not, unfortunately, extend the interpretation of their ideas in terms of molecular or other mechanisms.

Moser (*18*) sought some means of making the Charpy measurement an absolute quantity—something characteristic of the material itself. It had been recognized that dividing by the cross section of the specimen did not yield a constant value for pieces of differing shape. Moser took the lead that, inasmuch as the absorbed energy is absorbed in a volume of the material, a division by an area cannot be right, and that a true impact constant will be expressed as energy per unit volume. The problem then becomes one of determining the volume which participates in energy absorption. Moser further postulated that the volume which participated in energy absorption depended upon having the hammer speed below a value which he termed the "velocity of strain propagation" in the material. This is not the velocity of a sound wave; what Moser had in mind can be visualized as the maximum speed with which a deformation would spread, with the material being deformed still able to re-form into cohesive bonding. Ludwik (*16*) described the matter as an opposition between an internal viscous cohesion and a shearing force; the

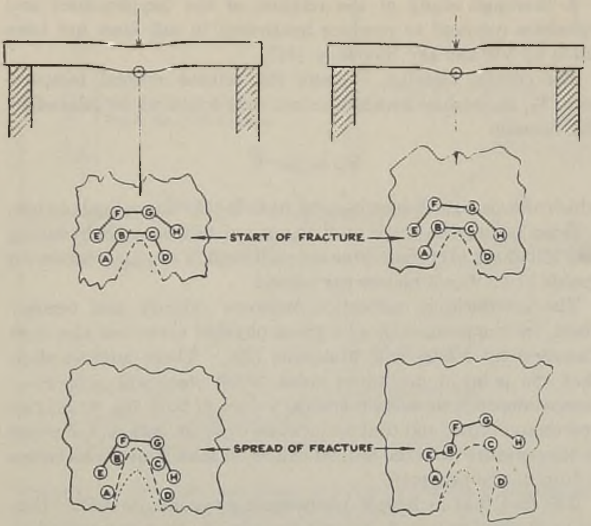


Figure 4. Effect of Heterogeneity in Bond Properties on Impact Strength

Brittle fracture—strain propagated in small volume with steep localized wave front, uniform relaxation times.

High impact resistance—strain dissipated over large volume in all directions—wide distribution of relaxation times.

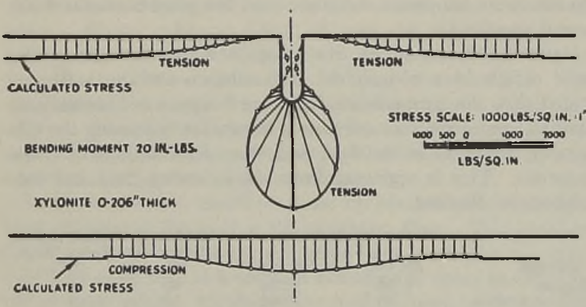


Figure 5. Principal Stresses at Surfaces of Notched Bar under Flexure (*6*)

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latter rises with the velocity of the blow; when it equals viscous cohesion, then, according to Ludwik, brittleness ensues.

These ideas were not precisely crystallized but presented two very useful concepts whose importance was not recognized because of the failure to define them in terms of recognizable structural features. These concepts are: (1) Maximum toughness is obtained when the material is such as to distribute the effects of the blow over a large volume. (2) This large volume is obtained when the material possesses the ability of rapid distortion without rise of the distortion to fracture.

We shall now see how such concepts can take on meaning in terms of structure. If we consider an inorganic crystal such as rock salt, a significant feature of the force bonds which hold the crystal together across any plane is their similarity to one another in type, in magnitude, in distance of extension, and in relaxation times. Once rupture starts, the breaking of such a crystal continues, in comparison to a polymer, like the dissolution of the "one-hoss shay" of Oliver Wendell Holmes, which was made to have every part as strong as the next; nothing more and nothing less.

When we consider, on the other hand, a plastic material composed of long chains which are unlike in length and perhaps in composition, and which are bound to one another in crystalline array in some parts and in others in a random amorphous manner, and when we consider further that they are interspersed with a plasticizer, then we have considerable opportunity for a wide distribution of bonding energies, of extensions, and of times necessary for re-forming after breakage.

Figure 4 shows how this degree of heterogeneity in these bond properties enters into impact strength. An unnotched beam, supported at the ends and struck in the middle, is shown at the top, and the beam is pictured just at the time the stresses have built up to where the first small fracture appears. This is pictured in an extremely magnified and schematic way. *A*, *B*, *C*, . . .*H* are points of origin of secondary-type bonds, idealized as lines connecting *A*, *B*, etc. Primary-type bonds, or main chains, are omitted for we are making the usual and accepted assumption that plastic flow and rupture phenomena are concerned mainly with secondary-type bonds. We consider the left-hand beam to be composed of material having bonds quite alike in force constants, relaxation times, and extensibilities, whereas the right-hand beam has bonds of great heterogeneity in these characteristics. We picture the stress rising and the bonds connecting *ABCD* as breaking. The crack will then tend to progress forward. In the left-hand beam the bonds either will not have time to re-form to new neighbors or will do so in a symmetrical fashion, allowing the fracture to propagate forward in the same direction and with a narrow or sharp front. As it comes to bonds *EFGH*, the process is repeated, and the fracture progresses as a brittle type, with high stress concentrations at the forward edge.

Consider the right-hand bar, with a distributed variety in the above-mentioned properties of the bonds. Upon breakage of bonds *ABCD*, *A* and *B*, having short relaxation times, can re-form quickly to new neighbors, *EF*. On the other hand, assume *C* and *D* to have long orientation or relaxation items; they require the attainment of a considerable amount of energy from thermal collision processes before they can be activated to re-form with new

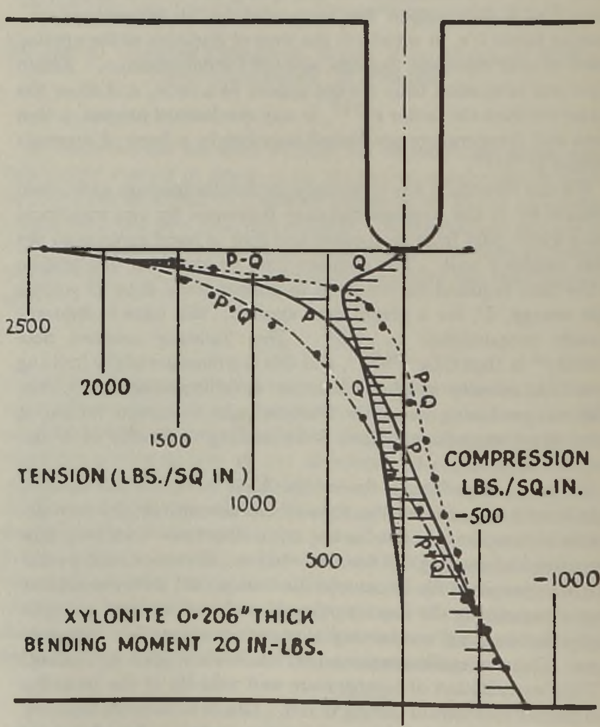

Figure 6. Stress Distribution in Notched Beam under Flexure (*6*)

COURTESY, MACMILLAN CO. & CAMBRIDGE UNIVERSITY PRESS neighbors. The side of the flaw with C and D is therefore opened up to the fracture which spreads out in this direction. Thus, the volume over which the force acts is increased and the stress concentration is reduced. Owing to the random distribution of "slow" bonds, such as C and D, as the fracture progresses it is dispersed in all random directions to produce a large available volume. Such a material is a tough rather than a brittle material. Such a material, as pointed out by Coker and Filon (*6*), is less subject to notch sensitivity.

While it is thus shown how heterogeneity of relaxation times leads to toughness, the same diagram and reasoning can be carried through by considering the bonds to have differing extensibilities.

This picture shows how increasing the velocity of the impact blow brings about the brittle type of fracture. One may picture the effect as a race between the advancing flaw and the relinking of separated chain segments. This relinking is determined by temperature and by activation energy; if these are held constant, increasing the impact velocity will cause the flaw to progress faster than relinking can dissipate it and check its advance.

EFFECT OF NOTCHES ON STRESS DISTRIBUTION

The common procedure of notching specimens has a useful value in building up stress concentrations, and hence approximating conditions met with in practice. Nearly all molded plastics have irregular outlines, projections, or indentations, or may acquire scratches in use. These discontinuities cause abnormally high stress concentration under loading, or even prior to loading, due to "frozen-in" stresses. Such stress concentrations bring the object much closer to fracture, so that the external force required for fracture is considerably lower than it otherwise would have been. Examples of stress concentrations are shown in Figures 5 to 8, as given by Coker and Filon (*6*).

Figure 5 shows the principal stresses at the surfaces of a notched bar which is subjected to bending. The upper part of the bar is stretched while the lower part is subject to compression. At the base of the notch, the stresses are about four times as large as would be obtained if no notch were present. Figure 6 shows the stress variation within the beam along section CD. As one moves from the surface of the notch, tension stress P, acting parallel to the beam length, falls off rapidly from a high value to zero and then changes to compression. This shows how important the very surface of the notch is—a fact already well known in testing laboratories. Stress Q acts in direction CD and is of lesser importance. Figure 7 shows the same type of thing for a V-shaped notch. In A the value of (tension) stress P at the very surface is plotted around the perimeter of the notch; it is always directed parallel to the surface. B shows the rapid drop in tension from the surface into the interior of beam along section CD. C shows how the principal stresses rise rapidly as the notch is cut sharper; this is in agreement with the common experience that sharp scratches, even if small, can lead to marked lowering of impact strength.

Figure 8 shows the distributions of the surface stresses (tensions) in the Charpy and Izod specimens. These surface stresses act parallel to the surface (in the plane of the diagram); their magnitudes are given by the length of the radial lines to the curve. Again, we note high stress concentrations at the notch bases. The Izod distribution is unsymmetrical toward the clamp. It has been found that the pressure of the clamp or vise causes further stress concentrations which can lead to abnormal results.

Coker and Filon (*6*, pages 596 and 599) state that the influence of the radius of curvature is more marked in a brittle material than in a viscous one, since in the former case the stress distributions can suffer little change as fracture progresses. They state that, as a quality test, a notch impact test may be too severe and reject good material because of the differing influence of notch radius according to the type of material being tested.

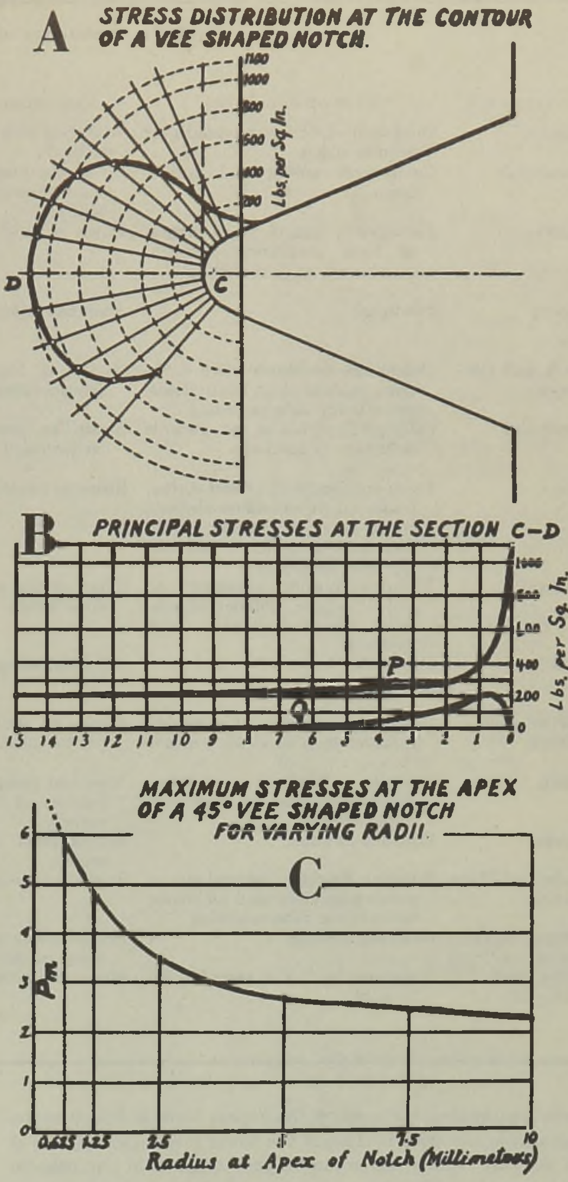

Figure 7. Stress Distribution for a V-Shaped Notch under Flexure (*6*)

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This concept is in accord with the picture which has been developed showing how a fracture may be propagated and how, for a brittle material, the propagation is in a narrow and directed manner. Coker and Filon draw attention to the maintenance of abnormal stress distribution in such a case. The concept of Figure 4 shows how such stress distributions can be lowered and dissipated by having molecular properties which lead to dissipation of force into larger volumes. We can also view this concept as increasing the radius of curvature of the progressing "flaw notch".

SHOCK WAVE PROPAGATION

Another phenomenon in impact testing is the generation and propagation of a shock wave or sound pulse, which travels through the material with the speed of sound and is reflected from the test-piece surfaces. In general, the speed of these pulses is

Table I. Summary of Newer Testing Methods

INVESTIGATOR	TYPE OF APPARATUS	VARIABLES MEASURED	TYPE OF SPECIMEN & DEFORMATION	COMMENTS
Albertoni	Pendulum—specimen released after definite strain	Absorbed energy as function of strain	Rod, bar, or ring tensile	Entirely mechanical; several readings necessary to establish curve
Brenschede	Compressed spring and optical beam	Linear compression (for constant pressure) as function of time	Cylinder; one-dimensional compressional	Suitable only for small deformations
Brinkmann	Falling-wt.; quartz piezo crystal as force measuring element; cathode-ray tube recording	Stress as function of strain	Rod tensile	With sufficiently large weight, strain rate can be made constant; good principle, limited only by height necessary to attain high velocity
Charpy	Pendulum	Absorbed energy at fracture	Notched or unnotched bar flexural	Simple in operation; too many parameters of material enter into result
Clark and Dätwyler	Pendulum—resistance wire strain gage calibrated to yield stress; cathode-ray tube recording	Stress as function of time (strain calcd. therefrom)	Rod tensile	Complete curve obtained in one test; neither stress nor strain constant
Elmendorf	Falling-wt.; stylus on wt. records deflection of specimen	Strain as function of time (stress calcd. therefrom)	Beam flexural	Complete curve obtained in one test; neither stress nor strain rate constant
Ginns	Force applied by displaced spring, measured by resistance-element strain gage (calibrated); strain measured optically; cathode-ray tube recording	Stress as function of strain	Rod tensile	Complete curve obtained in one test; neither stress nor strain rate constant
Itahara	Rotating flywheel engaging one end of hollow cylinder of material mounted co-axial with flywheel	Shear stress *vs.* function of shear strain	Hollow cylinder shear	Deformation reduced to simplest terms, pure shear
Izod	Pendulum	Absorbed energy at fracture	Notched bar flexural	Simple in operation; too many parameters of material enter into result
Körber and Storp	Pendulum extension of specimen recorded by photoelectric means	Strain as function of time (stress calcd. therefrom)	Bar flexural	Can be applied to ordinary Charpy or Izod apparatus; neither stress nor strain rate constant
Mann	Rotating flywheel; absorbed energy measured by pendulum displacement	Absorbed energy at fracture; velocity of impact can be varied	Bar tensile	Interpretation of results at high rates questionable
Myers	Rotating flywheel	Brittle point as function of velocity	Bar or strip flexural	Brittle point may be better suited for some service correlations
Nadai and Manjoine	Rotating flywheel; optical slit as strain gage calibrated for stress; cathode-ray tube recording	Stress as function of strain	Rod tensile	Complete curve obtained in one test; strain rate constant in test; can be given different values
Vitman, Selker, *et al.*	Rotating flywheel	Brittle point as function of temp. or velocity	Bar flexural	(See Myers)
Welter and Morski	Specimen, load, and recorder fall from ht.	Stress as function of strain	Rod flexural	Entirely mechanical recording; entire curve obtained in one test; neither stress nor strain rate constant

much greater than the speed of the impact blow, although at the high speeds now used in some of the newer investigations, this is not the case. Such waves can be photographed in photoelastic specimens (*7*). The damaging effect of such a pulse is related to its amplitude and steepness of wave front. As such a pulse passes over a point in the material where stress is already present, that of the pulse is momentarily added to it and may carry the stress over the limit for fracture. Complicated effects arise from the manner in which multiple reflections and constructive interferences may cause abnormally high momentary stress. Figure 9 illustrates some properties of these pulses. A high internal damping capacity is effective in reducing the amplitude and wave front of these pulses, and this, in turn, is related to the degree of heterogeneity of elastic moduli of the various bonds. For a material of uniform bond characteristics, the wave progresses uniformly. A material with heterogeneous moduli and relaxation times will cause a dispersion in velocity and dissipate the pulses. Reflection phenomena are discussed by Timoschenko (*22*), and the "damping capacity" of a material is presented by Lazan and Yorgiadis (*15*).

PROCESSING CONDITIONS AND INGREDIENTS

The well-known beneficial effect on impact strength of the addition of a plasticizer comes about because: (1) The energy required for the cohesive flow process to occur is lowered; this results in a decrease of the relaxation times with the effects illustrated in Figures 1 and 2. (2) The heterogeneity of bonding properties is increased, with the resultant change in the manner of fracture propagation, as illustrated in Figure 4. Also, notch effects are minimized and shock waves dissipated. Moisture adsorbed in the material also acts as cause 2.

To achieve this heterogeneity of bonding, it would thus appear that too intimate a mixing of polymer and plasticizer may not be desirable just as insufficient mixing is also to be avoided. A plasticizer which is very soluble in the polymer leads to too good a dispersion on a molecular scale. Dispersion must proceed to some degree which can be illustrated as follows: If by analysis the percentage of plasticizer could be determined on progressively smaller samples of a plastic, steady values would be found at first. As the size of the sampling volume was made very small, the percentage of plasticizer analyzed would be found to be erratic (assuming perfect analysis) because of the randomness of dispersion becoming apparent. Such a variation of composition should become apparent in volumes of the order of 100 to 10,000 cubic Å. to achieve a heterogeneity of relaxation times.

In the molding of an object, it is known that too low a temperature produces poor mechanical properties, because of insufficient

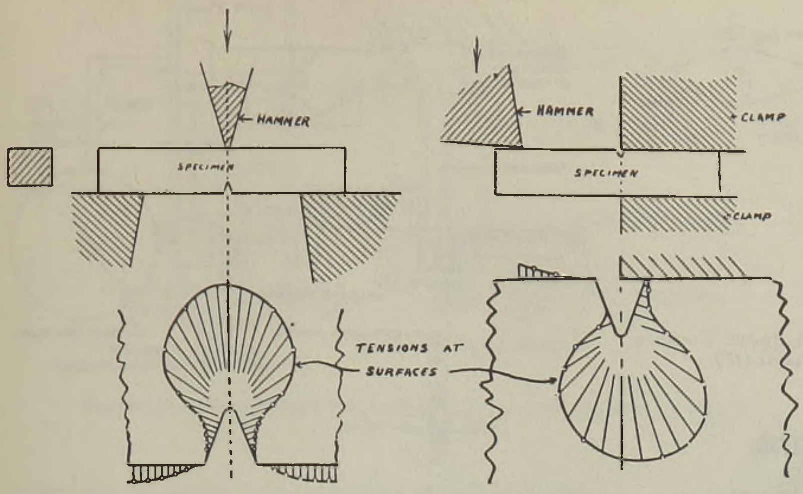

Figure 8. Stress Distributions at V-Shaped Notch in Charpy and Izod Type Mounting

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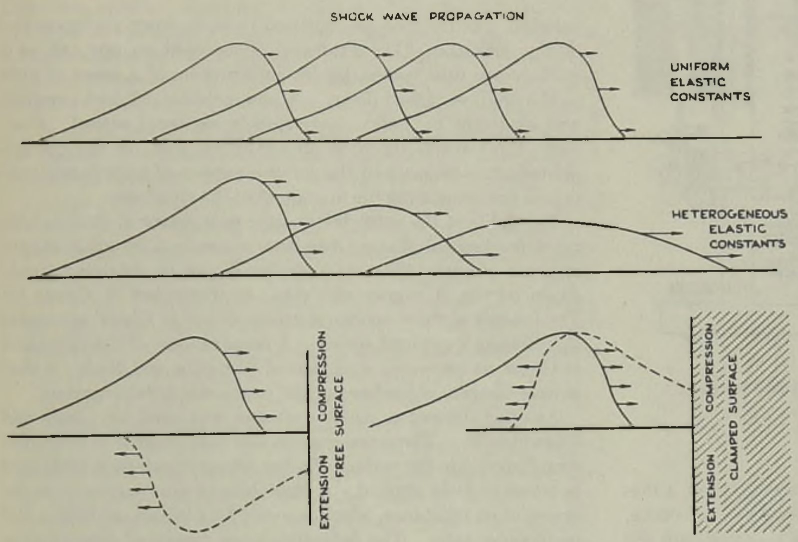


Figure 9. Properties of Sound Pulses

development of secondary bonds. In the flow process during molding, sufficient energy as kT must be available to activate the energies, U_i, of the various secondary bonds and effect cohesive bonding of the neighboring chain segments. Further molding effects relating to temperature are due to the relative amounts of crystalline *vs.* amorphous phases produced. Still another effect is the orientation of the chains and micelles of the material, induced by the hydrodynamic flow process of extrusion through small channels and orifices of the mold. Hence the surface of a molded object may have quite different characteristics from those of the interior; this is made evident by the "crazing" which develops upon immersion in a solvent. The section dealing with notches and stress localization emphasizes the importance of molding, buffing, or sanding the surface, and the importance of controlling the nature of the notch surface, particularly at its base.

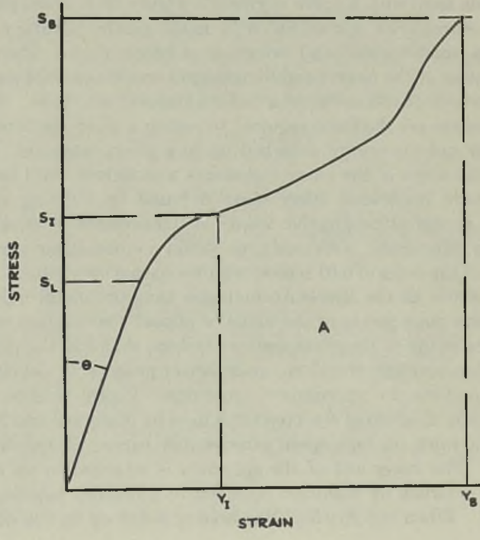
IMPACT TESTING METHODS

It is widely believed that if a test, such as an Izod, fails to correlate with service impact conditions, it will do so if sufficient refinements in technique can be applied. Thus, there are articles in the literature dealing with corrections for the kinetic energy imparted to the broken piece; articles dealing with a trial of various end points at which absorbed energy should be measured; and others dealing with the relative size of notch to that of test piece, etc. While work along these lines will in some cases improve the utility of the test, there may be cases where a lack of service correlation is made still more evident by such refinements. Reliable results will not be obtained generally as long as the common pendulum test is expected to furnish an all-inclusive impact parameter.

Laboratories which are fortunate enough to handle materials for which a service correlation is evident with an Izod test should continue its use but should make no attempt to read anything more into the test. Indeed, the originators of such tests had in mind no such interpretations; the difficulty has arisen as later workers, forced by lack of other means, have tried to read hidden meanings into the results of the Charpy or Izod tests.

Figure 10. Useful Parameters Obtainable from Complete Stress-Strain Curve

Area A
Tan θ
S_L = stress at linear unit
S_I = stress at inflection point
S_B = stress at break
Y_I = strain at inflection point
Y_B = strain at break
Each parameter is a function of temperature and strain rate.



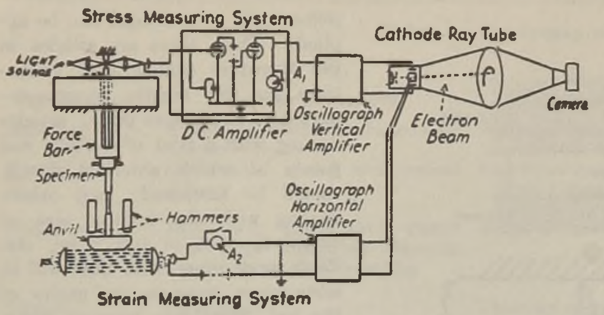


Figure 11. Recording Systems of High-Speed Tension Test Machine of Manjoine and Nadai (*17*)

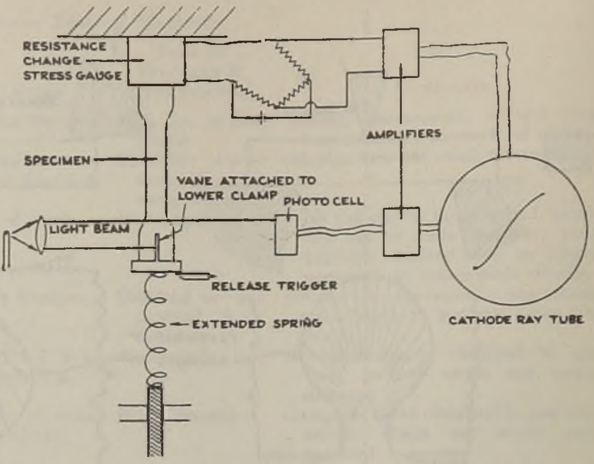


Figure 12. Schematic Arrangement of Apparatus Used by Ginns (*12*)

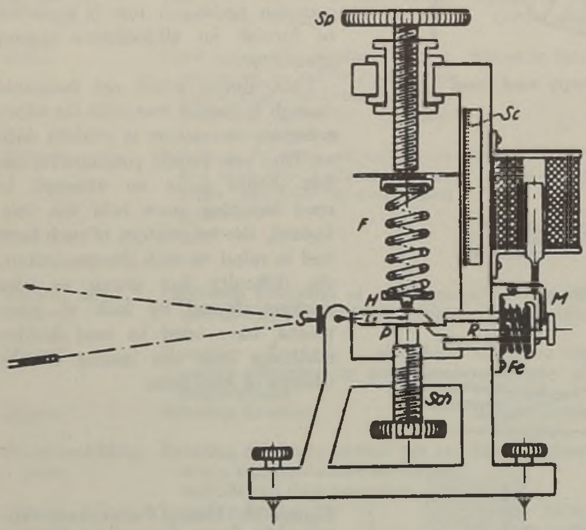


Figure 13. Device of Brenschede (*4*) for Impact Compressional Loading

Perhaps the most powerful single test for the study of a material under applied load is the complete stress-strain curve, where either stress or strain is increased by a machine until the specimen breaks. An illustration of the useful parameters obtainable from such a curve is given in Figure 10. These parameters characterize a material with much greater accuracy than do the breaking load and extension at break alone. Thus, the parameter of the usual pendulum impact test is absorbed energy. This is to be found as the area under a stress-strain curve. Other parameters are the force required to obtain a given specimen extension and the energy absorbed up to a given extension. Further, the slope of the curve represents a modulus. Still further and more important information is found by running stress-strain curves at progressive values of temperature or at several known time rates. Obviously, to obtain a stress-strain curve in times of the order of 0.01 second requires special apparatus.

A review of the literature indicates that the metal industry has been more aware of the value of impact stress-strain curves and the study of time-temperature factors, than has the plastics industry, and has, therefore, made better progress in developing and applying the appropriate apparatus. Figure 11 shows the schematic diagram of the apparatus used by Manjoine and Nadai (*17*) in work on high-speed stress-strain curves of copper and steel. The lower end of the specimen is attached to an anvil, which is struck by hammers attached to a massive rotating flywheel. When the flywheel has been speeded up to the desired velocity, the hammers are released to force down the lower end of the specimen. The extension is recorded on one axis of a cathode-ray tube screen, by the interruption of a beam of light as the anvil is carried down. A photoelectric cell and amplifier unit make the necessary conversion to electrical output. Similarly, the force is recorded on the other axis by the optical-photoelectric measure of the small extension of a previously calibrated bar supporting the upper end of the specimen.

The value of the cathode-ray tube as a means of dealing with rapid mechanical changes has been recognized by other experimenters. Ginns (*12*) used a similar device in obtaining stress-strain curves of copper and steel, as illustrated in Figure 12. The loading of the specimen is accomplished in Ginns' apparatus by releasing a strained spring. A disadvantage of the apparatus of Ginns, as compared with that of Manjoine and Nadai, is that neither the rate of loading nor the strain rate is held constant.

Another somewhat similar scheme was used by Clark and Dätwyler (*5*). The stress gage in this case consists of resistance wire fastened to the surface of a bar whose extension is calibrated in terms of force applied. A stretching of wire results in an increase of its resistance, which is noted by a bridge, amplifier, and oscilloscope tube. The deflection is not measured directly as in the devices of Manjoine and Nadai and of Ginns, but the oscilloscope beam is moved by a time-sweep circuit and the strains are obtained by calculation. The force is applied to the tup or anvil at the end of the specimen by a pendulum. Again, we have the disadvantage that neither stress nor strain rates are constant. Nevertheless, the method represents an advance in the study of impact measurements.

A device described by Brenschede (*4*) for subjecting materials to impact compressional loads is shown in Figure 13. The force is supplied by compressed spring *F* which is suddenly applied to specimen *P* upon release of trigger *R*. Since the compression of the sample is small, the force may be considered constant. An optical beam reflected from mirror *S* to a revolving photographic drum thus gives a strain-time curve for constant stress.

Figure 14 shows a completely mechanical device for recording the stress-strain curve, as developed by Welter and Morski (*26*). The specimen, with a weight at the lower end, together with the complete recording device, is dropped from a height, on guide bars, to an anvil. The decelerating force is measured by a spring in series with the specimen; the extension is measured by the rotation of a drum which falls with the specimen and is made to rotate by lugs on the bottom of the specimen engaged in a spiral groove in the drum.

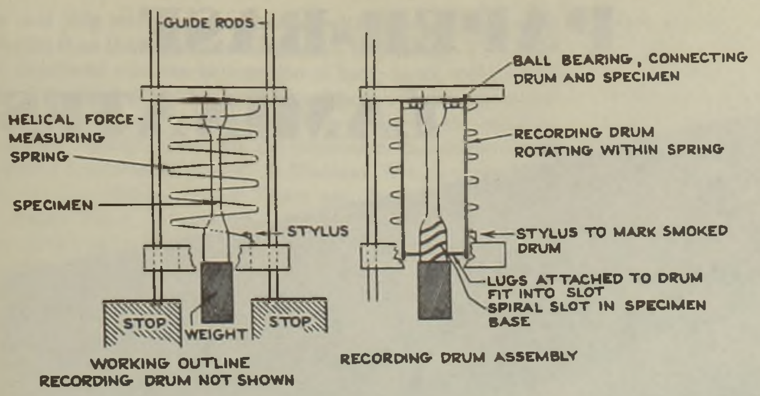


Figure 14. Mechanical Stress-Strain Impact Apparatus of Welter and Morski (*26*)

Table I summarizes the main features of some of the newer testing methods. Among them is a pendulum device, described by Albertoni (*1*), in which the energy absorption is measured as usual by the height of rise of the pendulum after the blow has been struck. However, the distortion of the specimen is not carried to the point of rupture as in the usual tests, but by a trigger release device the specimen is unclamped at the end of the desired extension. Thus, no further energy is absorbed, and a point is obtained on a curve of absorbed energy *vs.* extension. This curve can be plotted by using either the same sample or a number of different samples, and progressively increasing the extension to which the sample is subjected before release. The ordinate of absorbed energy can be transformed to one of force. For an elastic material such as rubber, the same specimen may be used over and over, but this is not justifiable with plastics; several specimens must be prepared and deformed to obtain one curve. Again, the loading and deformation rates are not constant. Brinkmann is reported (*17, 25, 26*) to have used a piezoelectric crystal as the stress-recording device and to have recorded the variables by a cathode-ray tube.

One of the earlier devices was described by Elmendorf (*8*). A falling weight, guided by tracks, struck the center of a beam supported at the ends. A stylus, fastened to the falling weight, made a mark on a rotating drum and thereby produced a graph of displacement of the center of the beam *vs.* time. By calculation from this curve, a stress-strain curve was obtained. There is a marked similarity between the methods of Clark and Dätwyler and of Elmendorf; both measure one coordinate directly as a function of a recorded time scale, and calculate the stress or strain therefrom. Thus, the Elmendorf method obtains, from experiment, strain as a function of time. A mechanical process of differentiating by taking the slopes of the curves yields the instantaneous velocity of the falling weight, and the process repeated yields its deceleration and, hence, the force applied to the specimen. On the other hand, Clark and Dätwyler obtain force as a function of time. The displacement of the pendulum is obtained by a reverse process of stepwise integration of the force-time curve to obtain velocity and finally strain as a function of time. The method of Körber and Storp (*14*) is basically the same as that proposed by Elmendorf. The blow is applied in this case by a pendulum instead of a falling weight, and the pendulum displacement is recorded by the interruption of a beam of light entering a photoelectric-cell. The displacement-time curve obtained can then be interpreted as a stress-strain curve.

Vitman (*24*) described a rotating flywheel with a tooth to engage the specimen. This apparatus did not measure either the force or the absorbed energy. Rather, the impact velocity was varied and the type of fracture examined. For a definite temperature, as the impact velocity is increased, a point is reached at which the specimen breaks in a brittle-type fracture. Also, for a constant velocity there is a definite temperature at which the brittle fracture is obtained. Using this brittle point as a criterion, velocity and temperature are related in some inverse manner for each type of material.

Myers (*19*) also made use of the appearance of brittle fracture as a criterion, the impact velocity being variable with a rotating flywheel. His paper shows that the notched Izod test sums and weights the basic factors differently and thus produces poor correlation between the two test methods.

CONCLUSION

It will be possible to make extensive correlations and predictions on impact behavior when data are at hand from stress-strain curves taken at a series of temperatures and impact rates, and, in addition, when we have data on bond relaxation heterogeneity obtained from electrical relaxation studies, from creep-curve analyses, or from studies of hysteresis or elastic recovery at varying temperatures. Such data when properly blended will be far superior to any obtained from a Charpy or Izod test.

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PAPER-BASE LAMINATES

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A development of considerable interest in the laminating field during the past several years has been the production of special impregnating papers which, in their final laminated form, yield better physical characteristics than those of the paper-base laminates of earlier years as developed for electrical purposes. The newer laminates are generally made from impregnated papers at pressures below 250 pounds per square inch with resin contents of approximately 35 to 40% where phenolic resins are used and under such conditions as permit their applications to both press and bag molding. This paper reviews the general development and presents information relative to the effect of variations in paper impregnation, in curing processes, in resins, and in laminating conditions on the characteristics and the possible uses of the laminate. A wide variety of thermosetting and of thermoplastic resins have been studied, and data covering the properties of laminates are presented.

Airplane Fuselage Constructed of Paper-Base Laminated Material

(Courtesy, Vidal Research Corp.)

THE description of any rapidly developing branch of technology is a hazardous undertaking, particularly when the developments are appearing only to a limited degree in the technical literature. This is the situation which faces the reviewer of the new field of low-pressure paper-base laminates. Improvements are continually being made in paper stock and in the papermaking processes; new resins or improved modifications of the old are appearing; increased fundamental knowledge is available concerning the relation between resin and fiber, and all combine to make any broad review of the subject not completely accurate in all its phases. The case of low-pressure paper-base laminates is further complicated by the fact that many of the applications are involved in war research, and information as to the behavior of the laminates for these uses is not available at present. Nevertheless, it is possible to present a fairly complete picture—somewhat outdated in a few places but, on the whole, serviceable. The data illustrating this review have been selected in part from the technical literature but, in general, have been taken from the research files of The Institute of Paper Chemistry.

The electrical industry may be said to be responsible for the use of resin-impregnated papers for lamination. In searching for suitable insulators, they introduced shellac in 1904 as a binder for fibrous laminations. Tubes were made from paper by coating one side with shellac and winding the product on a hot mandrel. Phenolic resins were substituted for shellac in 1910 and, after experimentation, superior products were developed for insulating purposes. Other uses were later developed for the same types of materials. Some were successful and others were superseded by better products.

The resins were either phenolics or ureas, the former being limited in use because of their inherent brown shades and color instability in ultraviolet light. The ureas permitted a wider range of colors, gave fast-to-light shades, and, for some purposes had better electrical properties than the phenolics. The phenolic laminates, however, were stronger and gave better water resistance and, hence, had a wide application. Over the years, although the specifications set up by the National Electrical Manufacturers Association had been maintained and followed, the manufacturers of electrical insulation and other laminates have been mindful of the possibility of improving the strength of their products and have constantly worked on this problem with interested paper manufacturers. In the late 1930's a sheet was produced of hemp fiber and pulp which gave laminates with much better tensile strengths than those specified for grade X insulation. War, however, interfered with the importation of hemp stock, and further research was initiated which had for its objective the preparation of a high-strength sheet from paper stocks available in this country. Productive research along this line followed in the laboratories of the Forest Products Laboratory at Madison, Wis., in cooperation with the Consolidated Water Power and Paper Company and the Riegel Paper Corporation. General papers covering the scope of this investigation were presented by Stamm (*8*, *9*). As the result of this work and developments on the part of resin manufacturers, paper laminates are now being made with tensile strengths double and triple those of the products so widely used by the electrical industry and with greatly improved flexural and compressive strengths. With suitable resins the molding operation may be carried out at pressures as low as 50 pounds per square inch with good results, and newer resins are available which require practically no pressure. The following table compares the strengths from the type X insulation and the new impregnated Mitscherlich spruce sulfite laminate. More recent products show even greater divergence in strength.

	Type X	Mitscherlich Cross Laminate
Specific gravity	1.35	1.34
Tensile, lb./sq. in.	12,500	23,700
Compression, lb./sq. in.	25,000	44,600
Water absorption, %	4.0	1.5

CAUSES OF IMPROVEMENT

In the first place it should not be assumed that the development has been an overnight discovery involving some new principle or product of nature. Although the work at the Forest Products Laboratory may have first publicized spruce Mitscherlich pulp, high-strength laminates have also been developed from rag stock and from kraft pulps. The production of a sheet satisfactory for this purpose results from a combination of conditions in both pulping and papermaking, and many of the variables which play a part have not yet been identified. Among the conditions controlled by the papermaker are the following: type of wood used, which controls fiber dimension and chemical components in the pulp; pulping and pulp purification processes, which control chemical composition, colloidal nature, and strength of fibers; and papermaking conditions, which control the physical structure of the sheet.

The resin manufacturer and converter, in turn, have other problems. The types of resins are important. Although the phenolic resins are generally assumed to be superior from the standpoint of overall characteristics among the thermosetting resins, they have little edge over the newer allymers and furanes, and the ureas and melamines are not far behind. Work has also been done with thermoplastic resins, and these yield products with certain desirable specific characteristics. Later in the discussion, data will be presented to show the characteristics contributed to the laminates by these and other resins. It is difficult to list at this point the various factors entering into proper resin behavior, since these depend upon the individual resins. The composition of the resin affects changes taking place on drying, storing, or pressing the impregnated paper. Likewise, the composition controls the course followed during impregnation, such as surface coating of the sheet, saturation of the voids of the sheet structure, and penetration of the lumen and fiber walls of the individual fiber. Finally, the molder, by varying the time, temperature, and pressure in his molding operation, may alter the characteristics of the laminates within certain limits.

Thus, we have a good illustration of a new product which, reflected against its publicity, might appear to be the result of one or two new and spectacular discoveries; in reality it must be considered to be the sum of a larger number of smaller discoveries or applications. Without any one or two of a number of given steps, the low-pressure paper-base plastic might never have been developed. The most important factors in the picture are probably the improvements in pulp and paper properties.

The favored wood is one which has long fine fibers and is relatively free of resinous extractives. Such a wood is best pulped by conditions resulting in a minimum of chemical and physical degradation. Spruce appears to be ideal for the purpose, but a number of other softwoods yield pulps of about the same characteristics. The Mitscherlich process of pulping has been widely used, but the kraft process can be made to yield as satisfactory a pulp, provided the papermaking conditions are altered to suit the pulp.

The most favorable stock conditions include those which result in a minimum of degradation and change in fiber dimensions, such as result from beating or wet storage (but these depend also on the pulp); forced drying beyond a certain point is likewise undesirable. Conditions affecting favorable sheet structure include formation, which should not be wild (otherwise fiber bundles will be present which are difficult to impregnate), high sheet density such as is influenced by wet pressing, and at the same time good porosity.

It is difficult to say what measurable physical characteristics may be used to evaluate the sheet for low-pressure lamination, short of going through the actual operation of impregnation and lamination. In general, the best sheets appear to have a high zero-span tensile value, a high apparent density, and a low Gurley porosity. This means a departure from conventional papermaking, since the usual sheet of high apparent density generally has a high Gurley porosity. In the conventional case density results from closing up the sheet by beating with the resulting increase in Gurley porosity. In early papers for high-strength laminates, a combination of low wet pressure and beating was applied to increase the density of the sheet and the laminate strength. It was then found that an increase in wet pressure made beating undesirable, and the densification of the sheet was obtained by high wet pressure alone. Such conditions do not of necessity apply to all pulps since, with kraft, it has been found that some beating along with a high wet pressure is desirable. Not all paper machines can produce papers of these specific characteristics from all pulps.

The effect of hand-sheet wet pressure as compared with laminating pressure is shown in Table I. Where possible, testing methods were those in Federal Specification LP 406a. Charpy impact determinations were made according to the A.S.T.M. methods.

IMPREGNATION

The zero-span tensile test of the paper measures, in a general way, the tensile strength of the fibers rather than the tensile strength of the sheet, which results from the tensile strength of fiber bonding. The value will not equal the tensile strength of the individual fibers because they are not all parallel, nor is a solid mass of fibers held in the jaws of the tester. The highest zero-

Table I. Effect of Hand-Sheet Wet Pressure Compared with Laminating Pressure (Mitscherlich Pulp)

Sample number	1		2	
Paper properties				
Wet pressing, lb./sq. in.	50		250	
Oven-dry content after pressing, %	33.4		52.0	
Apparent density, gram/cc.	0.56		0.71	
Gurley porosity, sec./100 cc.	8		83	
Specific tensile[a]	7,150		9,750	
Specific zero tensile[a]	19,300		20,300	
Laminate properties (phenolic resin content 40%)				
Pressure, lb./sq. in.	100	1000	100	1000
Specific gravity	1.22	1.41	1.38	1.43
Specific tensile[a]	16,900	18,900	19,200	21,600
Specific flexure[a]	19,400	22,900	21,600	23,100
Edge-notched Charpy, ft.-lb./in.	0.59	0.68	0.83	1.05
Extensibility, %	2.10	2.23	2.26	2.25

[a] These values are derived by dividing the tensile or flexural strength (in lb./sq. in.) by the specific gravity, thereby converting them to an equal weight basis.

Table II. Comparison of Strength of Laminates Made from Two High-Strength Papers (One with Grain, the Other without Grain)

Molding conditions				
Pressure, lb./sq. in.	75		75	
Temperature, ° F.	325		300	
Molding	Press		Fluid	
Specific gravity	1.35–1.40	1.35–1.40	1.34	1.34
Tensile strength, lb./sq. in.	Parallel	Cross	Parallel	Cross
Machine	36,000	25,000	26,200	22,400
Cross	18,000	....	21,700	....
Compression, lb./sq. in.				
Edgewise				
Machine	19,000	18,000	18,500	17,900
Cross	17,000	....	16,500	....
Flatwise	40,000	40,000	47,200	46,900
Flexure, flatwise, lb./sq. in.				
Machine	32,000	26,000	30,000	26,300
Cross	20,000	....	27,000	....

Table III. Effect of Lamination Pressure on Cross-Laminated Commercial Phenolic Impregnated Papers

	Rag Paper				Mitscherlich Paper		
Pressure, lb./sq. in.	20	100	250	1000	100	300	1000
Resin content, %	39	39	38	38	..	..	..
Volatile content, %	5.1	5.1	4.9	4.8	..	..	..
Specific gravity	1.02	1.16	1.27	1.41	1.35	1.39	1.40
Specific tensile strength	14,700	15,700	16,700	15,800	16,800	17,100	18,300
Specific flexural strength	22,300	22,000	21,500	24,300	18,100	18,900	19,700
Extensibility, %	2.20	2.93	2.52	3.07	2.06	2.10	2.04
Edge-notch Charpy impact, ft.-lb./in	0.69	0.96	1.16	0.98	0.59	0.61	0.64
24-hr. water absorption, %	7.5	3.4	1.7	1.2	2.47	2.02	2.06

span tensile of a paper sheet tested in this laboratory has been about 25,000 pounds per square inch. The tensile value of cellulose fibers is probably in the neighborhood of 80,000 to 100,000 pounds. The zero-span tensile strength of high strength papers produced commercially ordinarily runs between 12,000 and 15,000 pounds in the machine direction, although recently a paper has appeared which tests over 20,000. It must not be assumed that a sheet with a high zero-span tensile will always give a strong laminate, for too many other factors play a part in the ultimate product. Again, it should be said that, although such a sheet may behave well with a resin of the type of an alcohol-soluble phenolic, it may not be the best for some other type of resin with a different polymerization pattern and different flow characteristics. The impregnation of the paper sheet by an alcohol-soluble phenolic resin is performed in much the same manner as has been used since the early days of resin-impregnated papers. The process has been described in *Modern Plastics* (*1*). Drying is carried out at 285–295° F., and the dried sheet is then passed over an arch cooled with cold water in order to reduce the temperature to room temperature before winding. During this operation the resin is polymerized to a predetermined degree.

Factors which enter into the impregnating operation include the following: The first is the amount of volatile material to be left in the sheet. This is important in the pressing operation, for too low a volatile content interferes with the bond between the laminations, and at too high a volatile content excess solvent and other volatiles must be removed in the pressing operation if possible; otherwise the finished product will blister and delaminate. An optimum volatile content cannot be stated for all resins and papers. In general, with alcohol-soluble phenolics a volatile content of about 5% is satisfactory for molding at a pressure of 100 pounds per square inch. A second factor is the amount of resin left in the sheet. Insufficient resin gives poor water resistance, poor bonding, and poor appearance; too much resin makes for a brittle laminate with greatly improved water resistance. Facing sheets of higher resin content give good surfaces to cores of lower resin content. In general, satisfactory laminates are obtained with resin contents of 38–40% phenolic resin. Cox and Pepper (*2*) outline several theories dealing with the manufacture of laminates. They consider drying as the removal of the volatile materials (water, solvents, and resin intermediates) and at the same time the precuring of the resin. Such volatile materials are plasticizers for the resins and, therefore, the effect of both actions is to decrease the flow of resin. The authors find that the optimum drying corresponds to that required to give the minimum flow required to assure complete bonding. They state the problem as one of making bonds with a minimum amount of resin to fill voids, and they say the amount of voids is largely controlled by the type of paper, the pressure, and the moisture content. They determine the apparent density of the paper at the molding pressure used and from that calculate the voids as 38%, in fair agreement with the percentage of resin at maximum density (35% by volume). According to the void theory, the function of pressure is to reduce the amount of voids and permit the use of low resin contents. Papers for low-pressure molding must be of high density; otherwise, high resin contents would be required.

Two general procedures are followed in pressing: The first uses dies and hydraulic presses; the second uses the bag fluid pressure method similar to the Vidal process, the Duramold process, or some modification of these two. Because of the low pressures required, the use of inexpensive molds, such as those made from Kirksite (a zinc alloy) is possible, and fairly large sections may be molded. The disadvantage of the press method is that it ties up expensive equipment for long periods, and this emphasizes the desirability of developing quicker-curing resins or resins molding at very low pressures, such as the allymers. Bag molding permits the molding of large pieces, such as the section of the airplane fuselage shown in the illustration. With certain types of objects multiple molding may be practiced using the same form. The technical difficulties encountered in bag-molding large objects with impregnated paper have been largely overcome.

By modified papermaking conditions, it is possible to alter the ratio of the alignment of the fibers in the sheet so as to form, on the one hand, sheets in which the majority of the fibers are running parallel to the direction of the machine or, on the other hand, those in which there is a fairly even distribution in all directions. Certain characteristics of the laminates follow roughly the grain characteristics of the sheet. Thus, we can have paper with strong machine grain, giving laminates with much higher tensiles and flexures in the machine direction; and we can have other sheets where there is a more even balance in various directions in the sheet, giving laminates with lower strengths in the machine direction but better over-all strengths. These laminates appear to be more readily utilizable for purposes not requiring directional strength or for applications where cross lamination is impractical. Table II illustrates the characteristics of laminates made from these two general types of papers.

MOLDING CONDITIONS

A number of variables in the molding conditions influence the physical characteristics of the laminates. Among these are pressure, temperature, and time. The effect of increasing the pressure on the character of the molded product varies for different

Table IV. Effect of Curing Conditions on 40% Phenolic Commercial Paper

(Pressure, 100 pounds per square inch)

Press temp., ° F.	220	250	250	300	300	300
Press time, min.	20	10	20	10	20	30
Specific gravity	1.34	1.36	1.35	1.36	1.36	1.35
Tensile, lb./sq. in.						
Machine	25,100	25,400	28,400	28,200	28,200	28,600
Cross	9,500	10,500	14,200	17,000	16,300	16,800
Flexure, lb./sq. in.						
Machine	28,100	29,000	30,200	29,600	29,600	28,000
Cross	18,500	20,300	20,900	21,200	22,400	20,800
Edge-notched Charpy impact, ft.-lb./in.						
Machine	0.81	0.79	0.71	0.73	0.61	0.63
Cross	0.56	0.56	0.59	0.58	0.50	0.54
Water absorption, 24-hr., %	12.07	7.04	5.16	2.06	2.36	2.47
Acetone extract, %	30.4	12.9	8.0	0.9	1.0	0.7

Table V. Relation between Nature of Resin and Physical Characteristics of Paper Laminates

	Resin, %	Sp. Gr.	Sp. Tensile[a]	Sp. Flexural[a]		Sp. Compression[a]		Impact Charpy Notched, Ft.-Lb./In.		Johnson Shear, Lb./Sq. In.		Bond, Lb.	24-Hr. Water Absorption, %
				Flat	Edge	Flat	Edge	Flat	Edge	Flat	Edge		
100 Pounds per Square Inch Molding Pressure													
Phenolic	40	1.34	17,700	20,400	19,400	33,300	16,000	5.39	0.63	10,900	11,500	760	1.52
Furane	40	1.38	18,300	21,500	18,900	31,800	12,900	5.18	0.68	10,700	13,400	555	3.53
Allymer 149[b]	40–44	1.43	18,000	19,300	18,100	28,200	9,400	7.75	0.84	11,600	12,100	510	6.27
Allymer 39[b]	40	1.43	14,600	14,400	14,450	27,600	6,900	7.93	0.93	9,900	9,300	535	7.52
Melamine	60–62	1.47	11,200	13,600	11,300	25,600	16,000	1.51	0.47	7,900	9,800	870	3.38
Urea	60	1.35	9,900	12,500	13,250	25,000	14,200	1.72	0.47	6,600	10,500	735	2.00
Ethylcellulose	60	1.20	10,800	13,300	7,900	19,000	4,600	9.52	1.48	6,300	5,900	335	4.73
Vinylite XYNC	38–40	1.15	11,400	11,750	13,500	28,400	5,700	11.8	1.48	6,700	6,100	300	14.0
1000 Pounds per Square Inch Molding Pressure													
Phenolic	41	1.41	17,800	20,900	19,300	30,500	16,000	6.78	0.86	11,600	12,400	800	1.44
Urea	57	1.47	12,400	15,800	13,900	26,500	14,700	1.93	0.45	9,500	12,000	800	2.22
Melamine	61	1.49	11,900	15,700	12,100	31,000	16,000	1.67	0.49	7,700	12,600	930	2.11
Vinylite	43	1.27	10,400	10,300	12,250	23,100	6,800	11.70	1.30	6,800	6,400	375	11.02
Furane	41	1.42	17,700	18,900	19,000	32,800	13,700	5.12	0.71	11,600	13,900	640	4.29

[a] Derived by dividing the strength figure (in lb./sq. in.) by the density, thereby converting them to an equal weight basis.
[b] Pressed at 1 to 5 pounds laminating pressure.

types of resins and papers, as will be demonstrated later. In general, pressures of 1000 pounds per square inch yield only slight improvements in specific tensile, flexural, and impact strengths with phenolic resins (Table III). Urea resins, on the other hand, show a considerable increase in tensile, flexural, and compressive strength when molded at 1000 pounds. The optimum temperature of pressing depends upon the nature of the resin and the amount of catalyst in the resin. No fixed temperature can be set for resins in general, but 300–325° F. is ordinarily used with phenolic resins (Table IV). The time required is likewise determined by the nature of the resin, the amount of catalyst, and the temperature. The nature of the resin has a great influence on the physical characteristics of the laminate. In general, it may be said that the thermosetting resins are better adapted to low-pressure paper lamination than are the thermoplastic resins. One reason is that a resin with a low degree of polymerization may be selected which penetrates the sheet voids and effectively protects the cellulose surfaces. The low-molecular form is then polymerized by curing and hot pressing to a stable high-molecular form. Such thermoplastic resins as have been tested, on the other hand, are made either from natural high-molecular polymers, which penetrate the sheet structure with difficulty, or are produced synthetically by a process which does not lend itself readily to polymerization under the conditions of application. Thus, thermosetting resins tend to give better moisture protection than the thermoplastic resins. At the same time they are much more inclined to be brittle, and laminates made from most of the thermoplastic resins will have higher impact strengths.

A large number of resins have been studied in this laboratory: phenol-formaldehydes, allymers, urea-formaldehydes, melamines, and resins of the furane type. The thermoplastic resins studied include polyvinyl resins such as the alcohol, acetate, butyral, chloride, and their copolymers, cellulose acetate and other esters, cellulose ethers such as ethylcellulose, chlorinated rubber, methyl methacrylate, etc. Table V gives comparative strength data for the more interesting products, all of which were made with the same Mitscherlich sulfite sheet.

LOW-PRESSURE PAPER-BASE LAMINATES

Field (*4*) presented strength data for phenolic paper laminates determined at −70°, +78°, and +160° F. Table VI shows his data for sample P-3. The data indicate a lowering in compression strength as the temperature goes from −70° to +160°, and a lowering in tensile and flexural strengths. Shear strength is less for +78° than −70° F., but from that point on, it seems to lose very little if any. Impact strengths (not included in Table VI) are about the same at the different temperatures. A later paper by Sang and Field (*7*) presents additional data. Thus, it appears that paper-base plastics might be expected to possess higher strength at low temperatures and lower strengths at high temperatures with little or no effect on impact and relatively small differences in shear values between room temperature and high temperatures. Field also studied the compressive and tensile directional properties of paper laminates and concludes that the paper-base laminate is isotropic; i.e., it has approximately the same strength in various directions (when tested flatwise). This is in direct contrast to glass-base laminates which show their minimum strengths at a 45° angle between the stress and shear.

Marschner (*6*) describes many of the characteristics of high-strength paper phenolic laminates and reviews uses for these products. Among the latter are a gunner's seat, a turret part, a gun cover assembly, and ammunition boxes. The author presents charts which show the tensile properties and elastic modulus through a complete range of angles to face grain of paper-base laminates.

A number of articles have discussed the comparative strength of high-strength paper laminates and other materials, such as plywood, stainless steel, and aluminum alloys. Table VII gives comparative data for these products. Sang and Field conclude in this connection that the specific flexural values of high-strength paper-base plastics, as well as the specific tensile strength of the plastics, compare favorably with those of aluminum alloy, whereas the specific bearing strength is low and the specific com-

Table VI. Variations in Strength Characteristics of High-Strength Laminates with Temperature Variation (in Pounds per Square Inch)

	−70° F.	+78° F.	+160° F.
Compression			
With grain	26,530	19,800	15,300
Cross grain	26,850	20,650	15,100
Tensile			
With grain	27,450	21,000	13,400
Cross grain	24,800	20,830	12,920
Shear, flatwise			
With grain	17,350	11,550	10,900
Cross grain	16,550	11,930	10,800
Flexural			
With grain	30,300	22,660	17,800
Cross grain	33,050	21,820	17,000

Table VII. Comparison of Physical Characteristics[a] of Phenolic Resin Paper Laminates with Other Structural Materials

	Sp. Gr.	Sp. Tensile	Sp. Compression	Sp. Modulus of Rupture
18-8 steel[b]	7.85	23,600	23,600	3,000
Al alloy 24 S-T[b]	2.8	23,200	23,200	8,300
Mg alloy J-1h[b]	1.8	25,000	25,000	13,900
Paper laminate				
Cross laminate	1.38	22,000	16,000	15,700
Parallel laminate	1.38	29,000	16,000	21,000
Glass cloth[c] allymer 149	1.75	30,600	31,100	27,400
Plywood, 3-ply 0.070 in.[b] (mahogany-poplar-mahogany)	0.56	14,000	....	36,500

[a] Specific ultimate tensile strength and specific compressive strength are equal to the absolute values divided by the specific gravity; specific modulus of rupture represents the modulus divided by the square of the specific gravity.
[b] Dickerman (*3*, page 34).
[c] Strain (*10*, page 170).

pressive strength is much lower than for the aluminum alloy. They also conclude that the modulus of elasticity is not sufficiently high, which results in inferior buckling ability in curved sheet form. Some work has been published on fatigue behavior of paper laminates, but there is still much to be done, or possibly much to be published. Field tested paper-base laminates by means of the Krouse fatigue machine. In this machine a cotton laminate failed after 250,000 cycles and a stress of 75 pounds per square inch, and one paper laminate with a decided grain failed after 1,300,000 cycles and a stress of 85 pounds; its cross-laminated sample exceeded 2,000,000 cycles at 7,000 pounds. Field also pointed out that plastics have better damping capacities than metals, and this results in an increase in temperature within the material. Since the plastics have poor thermoconductivity, this heat is not dissipated; as a result, there is a greater temperature rise within the plastic for the paper laminates than for glass-cotton laminates. The above data were largely based upon an empirical testing procedure. Lazan (*5*) conducted fundamental studies of the dynamic properties of various materials, including plastics, and the interested reader should consult his papers.

Low-pressure paper-base laminates have many desirable characteristics. They combine strength and lightness and, for many uses, appear to be satisfactory. Brittleness and low yield strength need to be remedied for wide acceptance. They may be improved in the future by developments either in the paper field or in the resin field. Another way to overcome the undesirable characteristics would be to laminate the paper to other substances having high impact and yield and balance the other characteristics. This would involve combinations of paper and wood cores, paper and veneer, paper and metal foil, or combinations of the three. Investigations in these directions undoubtedly will result in new and improved products, and preformed housing sections, furniture, automobile, railroad car, boat, and airplane construction, radios, and many other fields will profit.

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[End of Symposium]

DIELECTRIC HEATING

Application of Dielectric Measurements to Cellulose and Cellulose-Filled Phenolic Laminating Materials

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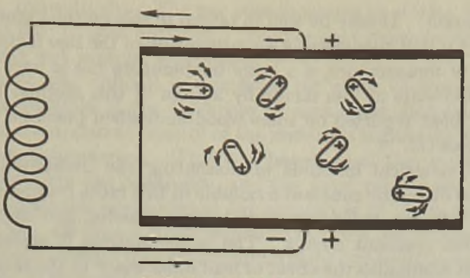
An attempt is made to outline some principles of dielectric heating and methods of applying dielectric measurement data to the solution of engineering problems in dielectric heating. Measurements of loss factor and dielectric constant in the radio frequency range for some cellulose-filled laminating materials are presented. A few of the problems of quantitatively attacking the problem of dielectric heating are sketched.

As any field of engineering develops, a set of rules, principles, and data accumulates which tends to eliminate the uncertainty and labor involved in the more direct approach of trial and error. The purpose of this paper is to discuss a few of the principles which must be considered in dielectric heating of materials, and to present data on the dielectric properties of cellulose-filled phenolic laminating material which should be useful to the engineer when he is dielectrically heating them. These data will tell him, for example, why, with the same voltage applied, they warm faster on some days than they do on others.

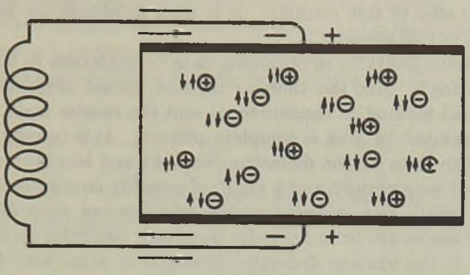
Dielectric heating is frictional heating, since it arises from the frictional heat generated within a material by the forced oscillatory rotation of molecules or parts of molecules, or by the forced oscillatory translational motion of ions (Figure 1). The driving force is an electric field, and the molecules, in order to be affected, must necessarily have an electric dipole moment or separation of positive and negative charges within them. Since the phenomenon is molecular in nature, the heating is necessarily uniform throughout, provided the material has the same molecular nature throughout and provided the electric field strength is uniform. If either of these varies, the amount of heating will vary. The amount of heating per unit time will depend upon the gross amount of rotation of the molecules or translation of the ions and the fraction of the total time they are in motion. It is thus obvious that alternating the electric field in sign and increasing the frequency of this alternation will greatly increase the heating by increasing the amount of rotational motion of the molecules. But this increase in frequency has much less effect upon the heat from the translational oscillation of the ions, unless they are restricted in the distance they can move in the direction of the field, before the electric field reverses and they move in the other direction.

The heating per unit time is also dependent upon the force (the electric field strength or voltage gradient) producing the rotation and oscillation. For reasonable voltages, unless there is a large concentration of ions, the amount of heat produced per unit time in dielectrics does not become appreciable until the frequency of the alternations of the electric field becomes of the order of magnitude of a million times a second. This means that, for materials having a low ionic conductivity, most of the heating must be produced by rotating dipolar molecules.

To translate these qualitative considerations into quantitative practice, each dielectric material can be characterized under any particular environment by two numbers, the dielectric constant ϵ',



DIPOLE ROTATION



IONIC OSCILLATION

Figure 1. Sources of Dielectric Heating

and the dissipation factor, tan δ. These two quantities are functions of temperature, concentration of impurities, and frequency. They are combined in another quantity, loss factor ϵ'', which is the product of the dissipation factor and the dielectric constant. The loss factor for a material determines the amount of heat which will be generated within it for any given voltage and frequency. The relation of heat generation to all these quantities is given by the equation:

$$5/9.E^2 f\epsilon''.10^{-12} = \text{watts/cc.} \qquad (1)$$

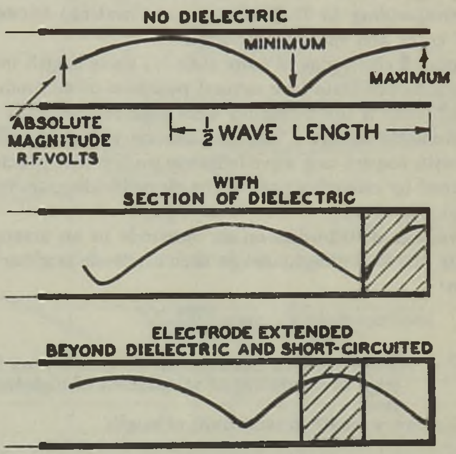
where f = frequency
E = voltage gradient, volts/cm.

This is a simple equation and may be made even simpler by considering frequency in megacycles (million cycles) per second and voltage in kilovolts. Then the factor 10^{-12} may be dropped. The loss factor for materials which are successfully heated is of the order of magnitude of 0.1 to 1.0 above one megacycle. If a material has a high concentration of freely moving ions, it may have a considerably higher loss factor at lower frequencies; but the product of the frequency and loss factor may be very low at those frequencies. It is often overlooked that the triple product of the frequency and loss factor and $5/9 \times 10^{-12}$, which is the conductivity, σ (in reciprocal ohm centimeters) is, for ionic conduction, essentially independent of frequency except for second-order effects and at low frequencies. In heterogeneous materials where there are closely spaced barriers to the ionic motion, there will, however, be a dependence of conductivity upon frequency and voltage.

The parameters which describe the dielectric properties of materials have been studied for many materials over wide ranges of frequency and temperature. Unfortunately a large majority of these data have been taken at low audio frequencies where various types of bridges may be used. There is a great need for more exhaustive data to be taken at frequencies above one megacycle.

It has been established theoretically and experimentally that all materials which have rotatable dipolar molecules display, at some frequency or frequencies, one or more peaks in their curve of loss factor *vs.* frequency. A similar peak also occurs in the curve of loss factor *vs.* temperature. In some materials at certain temperatures, such a peak occurs in the radio frequency region, and is of some importance to the dielectric heating of the material. Such a peak occurs at room temperature around 10 megacycles for cellulose and cellulose-containing materials (*8, 9, 10*). At higher temperatures these peaks shift to higher frequencies. In the same frequency range where such a loss factor peak occurs, there is a decrease in the dielectric constant with increasing frequency; the rate of decrease of the dielectric constant is directly correlated with the sharpness of the peak in the loss factor.

For plastic and semisolid materials these loss factor peaks are usually quite broad; they extend over several or more decades of frequency and in many cases will be almost flat. The theoretical interpretation of such loss factor peaks has been discussed in detail in the literature on dielectric behavior; suffice it to say here that it is related to the internal viscosity restraining the rotation of the dipolar molecules. A maximum in the loss factor will occur when the rotating molecules or parts of molecules, such as in polymers, can just keep up with the alternations of the electric field.



MEGA-CYCLES FREQUENCY	¼ WAVE LENGTH, AIR	1/16 WAVE LENGTH, $\epsilon' = 4$
1	246.0 FT.	30.7 FT.
2	123.0	15.4
5	49.0	6.15
10	24.6	3.07
20	12.3	1.54
50	4.92	.61
100	2.46	.31

Figure 2. Voltage Distribution

Unfortunately some investigators have placed undue emphasis on these loss factor peaks, believing that the frequency where they occurred was the optimum for heating the material dielectrically. It should be pointed out that the product of the loss factor and the frequency (Equation 1) continues to increase with frequency beyond the frequency where the loss factor maximum occurs; if the maximum is broad, the rate of increase of the product $\epsilon''f$, which will here be designated as the heating factor, hardly diminishes at all as the frequency is increased well beyond the frequency of maximum loss factor. It is thus evident that the higher one can go in frequency, the more watts will be converted into heat within the specimen for a given voltage. The frequency of operation is limited, however, by the state of development of oscillators with appreciable power output at higher frequencies, especially above 50 million cycles. It is likely, however, that wartime developments will lead to high power oscillators at well above this frequency.

Another factor limiting, to some extent, the application of higher frequencies is the voltage distribution and, thereby, the heating distribution to be encountered when the dimensions of the electrodes which are applied to the sample become an appreciable fraction of $^1/_4$ wave length. A quarter wave length at 50 megacycles is 4.92 feet in air; and with a material having a dielectric constant of 4 between the electrodes, this $^1/_4$ wave length will be reduced to 2.46 feet, since the wave length varies inversely as the square root of the dielectric constant of the medium. The shortening of the wave length in the region of the dielectric is illustrated in the second diagram of Figure 2. If the electrodes are fed at 50 megacycles by leads from one edge and the distance to the other edge is 2.46 feet, the voltage between the electrodes will vary sinusoidally from almost zero where the lead is attached to a maximum value at the opposite edge. The electrodes, to minimize this standing wave effect, must be less than $^1/_{16}$ wave length in the region of dielectric from the point of entry of the high-frequency lead to the farthest edge. This is an arbitrary figure at which there is only 8% variation in the voltage (corresponding to 15% variation in heating) between the point of entry and the farthest edge.

In Figure 2 electrodes of more than $^1/_4$ wave length in extent are shown to illustrate how several positions of minimum voltage could occur if the frequency were high enough with respect to the electrode extent. The situation on electrodes relatively shorter with respect to a wave length is simply that which would be obtained by removing part of the electrode diagram from the left-hand side.

The voltage distribution on an electrode in an arrangement with only one lead attachment to each electrode is given by the equation:

$$V \stackrel{\frown}{=} V_{max} \cos \frac{360x \sqrt{\epsilon'}}{\lambda} \tag{2}$$

where V = voltage between electrodes at distance x from farthest edge to wardpoint of attachment of high-frequency lead
λ = wave length in same units of length

The angle in the equation is expressed in degrees. In an electrode fed symmetrically from all sides by the high frequency, the condition is improved. In this case the highest voltage appears between the center of the electrodes and the lowest voltage between the edges. In such a case the voltage distribution is given by the equation:

$$V = V_{max} \left(1 - \frac{\pi^2 \epsilon'}{\lambda^2} r^2\right) \tag{3}$$

where V is the voltage between the electrode at a distance r from the center, if r is less than $^1/_8\,\lambda$.

By the proper use of tuning stubs to shift the position of the standing wave on the electrode in the region of dielectric, the situation can be improved (*2*). The effect of a single tuning stub is illustrated in principle by the lower diagram of Figure 2.

RADIO FREQUENCY MEASUREMENTS

The most usable range for the dielectric heating at present, for the reasons outlined briefly in the preceding paragraphs, is from 1 to 50 million cycles per second, which extends from the radio broadcast band up through the many short-wave bands used for foreign, amateur, and commercial transmission. One of the first methods of making dielectric loss factor measurements, many years ago, was the utilization of dielectric heating. The temperature rise in a given time at a fixed high-frequency voltage was measured in the material which was well insulated thermally. Then the loss factor was calculated from Equation 1. For the most part, this procedure has been abandoned in favor of electrical methods which are usually less time consuming and more exact. It may be well to return to this method more generally for it will give directly an integration of the loss factor over a range of temperature, if a large temperature rise is used. Some measurements of loss factor by a form of this method have recently been reported on some wood-flour-filled phenolic molding materials (*7*).

The electrical methods of measuring the dissipation factor and the dielectric constant available in this radio frequency range are as follows: radio frequency bridge, Q meter, and susceptance variation resonant circuit. The latter method is preferred because it eliminates the effect of lead inductance to the sample and of stray capacitance, which are usually present in the first two. This method was developed by Hartshorn and Ward (*5*) in its present form and is generally in use in the dielectric measuring laboratories of this country; it is used to obtain the data presented in this paper.

It seems desirable in obtaining data on materials to be heated dielectrically that the thermal method should supplement the electrical method of measurement and the results from the two be correlated to give a complete picture. It is usually desired to obtain data on the dielectric constant and loss factor over a range of temperature and a range of possibly encountered conditions. With this information the engineer can most efficiently couple the power from his radio frequency oscillator to the load, which is the heating dielectric arranged in some way between two high-voltage plates. Since the dielectric constant and the loss factor are likely to change during the heating cycle, it will usually be necessary for the operator to adjust continuously, either manually or automatically, the capacitance in his oscillatory circuit to compensate for these changes in the character of the load. Where the piece being heated is very small compared to the power available in the oscillator, this is not important; but in heating large pieces the adjustment is critical and may mean the difference between heating the piece successfully or not. With accurate data on the material and a knowledge of the voltage delivered by the oscillator continuously throughout the heating cycle, it should be possible to calculate the temperature rise in the sample. This desirable state has not yet been perfectly realized but is being approached.

LAMINATING MATERIALS

The materials reported from this investigation are typical commercial unbleached and unsized cotton duck, kraft paper, and alpha paper. Data on kraft pulp sheet, because of the similarity to those of the kraft paper, are omitted. These materials were taken from paper mill rolls and were not purified. Since in commercial practice the impurities are equally as good as the pure material in changing the loss factor and thereby the heating, it is better for this reason always to measure the material as it is likely to be used in practice. Not doing this has led to some disconcerting results. These same materials were measured after impregnation with B-stage phenolic resin in the case of the cotton duck (45% resin), and cresylic acid resin in the case of the kraft (43% resin) and alpha paper (64% resin). These sheets were actually taken from a production run in the manufacture of laminated plastic sheets. No other filler than the cellulose materials was present.

MEASURING TECHNIQUE

The susceptance-variation measuring device requires a 2-inch disk sample about $^1/_8$ inch thick; therefore a number of the thinner 2-inch-diameter sheets were stacked up to make $^1/_8$ inch. The moisture content of the samples was controlled by placing them in humidifying chambers previous to measurement. They were then removed and quickly measured, this operation requiring less than a minute; it was assumed that their moisture contents had not changed in this time. Measurements were made on samples humidified at 98%, 75%, 42%, and 15% relative humidity, respectively. The per cent moisture by drying these samples at 100° C. was obtained. The per cent moisture on the basis of the wet sample is reported.

Because it was difficult to compress the stack of sheets exactly to a multiple of the thickness of each sheet between the electrodes, the apparent density of the materials is given as it was during the measurement. This was based upon the weight of material between the electrodes, and the total volume between the 2-inch-diameter electrodes at the separation of the measurement. Thus, all the air space between the fibers, as well as the small amount (several thousandths of an inch) between the individual sheets, is included in this apparent density. This is an important consideration, for the apparent dissipation factor and dielectric constant will depend upon this apparent density, which is determined by the amount of compression of the material. The true density of cellulose fibers is variously reported in the literature to be between 1.45 and 1.60. The true density of the alpha paper and the kraft paper fibers was measured by displacement of the air with benzene in a pycnometer. They were dried under vacuum with a desiccant at room temperature previous to this measurement. The densities are: alpha paper fiber, 1.52; kraft paper fiber, 1.495.

From these values and the per cent water taken up, it is possible to calculate the true density at higher humidities. A slightly higher density for the adsorbed water was assumed according to the data of Maas (*6*). From the true density of the fibers and the apparent density of the material, it is possible to calculate the fraction of the total volume occupied by the solid material and the fraction occupied by the air space.

Measurements at higher temperatures were made in the same type of apparatus in an air thermostat. It was previously determined with a thermocouple at the center of a stack of sheets, that the temperature of the center came up to that of the electrodes after about 4 or 5 minutes. The distance to the center was about 1/16 inch from the electrode face. Therefore, about that amount of time was allowed for the sample to come to tem-

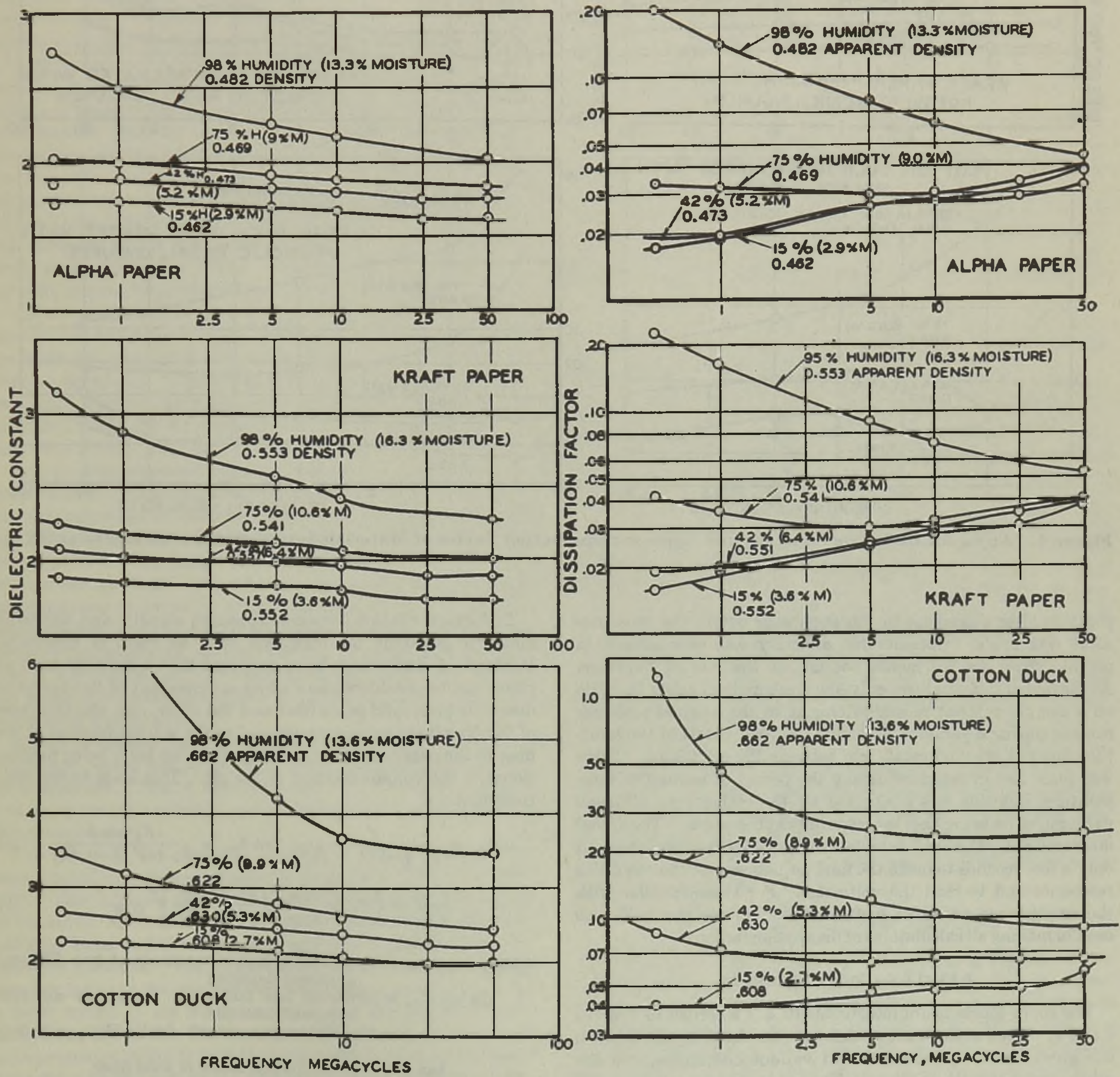


Figure 3. Apparent Dielectric Constant and Apparent Dissipation Factor of Alpha Paper, Kraft Paper, and Cotton Duck at 28° C.

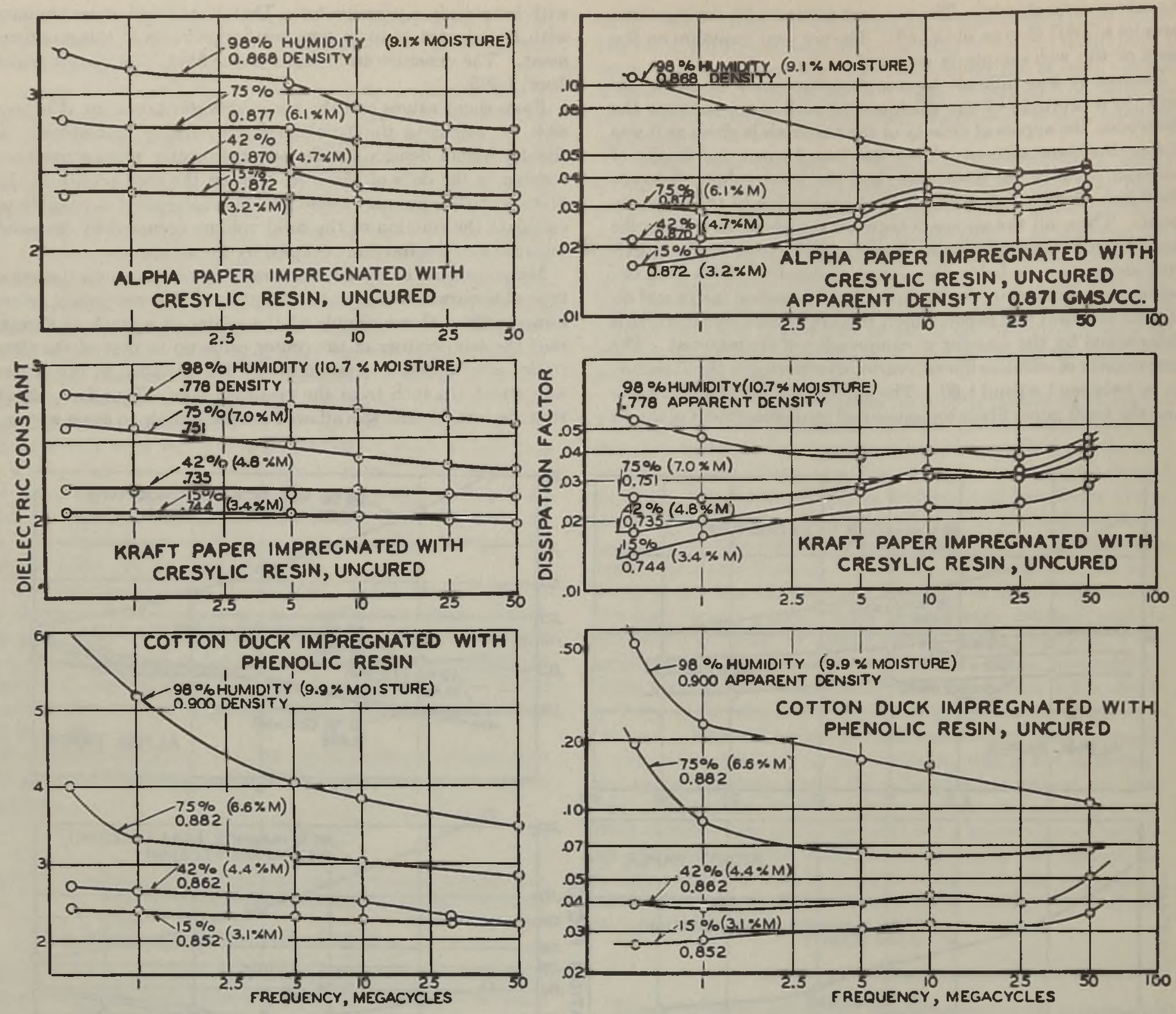


Figure 4. Apparent Dielectric Constant and Apparent Dissipation Factor of Materials Impregnated with Resins at 28° C.

perature after placement in the apparatus before the measurement was made. Considerable difficulty was encountered in making these measurements because of the loss of moisture. At the higher temperatures only one measurement could be made on a sample without reconditioning it to the original moisture content during a period of 24 hours. Actually most of the moisture was lost after removal from between the electrodes. There was some loss in moisture during the period of coming to temperature, but this was minimized by the rather long diffusion path, moisture being able to escape only at the edges. The actual measurement after the sample reached temperature required only a few seconds to make the final adjustment of the circuit to resonance and to read the voltmeter. For those familiar with the susceptance variation method, the "voltage method" was used in making all calculations of dissipation factor.

RESULT OF MEASUREMENTS

The room temperature measurements are recorded in Figures 3 and 4. Each of the six materials is represented by two figures; one gives the dissipation factor at various humidities, and the other, the dielectric constant. These are apparent values and will increase if the apparent density is increased.

The exact relation between apparent density and apparent dielectric constant for materials such as these is uncertain. Buchner (*4*) and others have proposed that a material such as paper can be considered as a series arrangement of two layers of dielectric (one, solid paper fiber and the other, air), the thickness of the fiber layer being proportional to the volume fraction of the fiber in the paper and the thickness of the air layer being proportional to the volume fraction of the air. This leads to the relations that

$$\epsilon'_{m_1} = \frac{\epsilon'}{F_1 + \epsilon'(1 - F_1)}; \quad \tan \delta_{m_1} = \frac{F_1 \tan \delta}{F_1 + \epsilon'(1 - F_1)} \tag{4}$$

$$\frac{\epsilon''_{m_1}}{\epsilon''_{m_2}} = \left(F_2 + \frac{\epsilon'_{m_1} F_1 (1 - F_2)}{1 - \epsilon'_{m_1}(1 - F_1)}\right)^2 \frac{1}{F_1 F_2} \tag{5}$$

where $\epsilon'_{m_1}, \epsilon'_{m_2}$ = apparent dielectric constants at two different apparent densities
$\epsilon''_{m_1}, \epsilon''_{m_2}$ = apparent loss factors at these two different apparent densities
ϵ' = true dielectric constant of solid fiber, excluding air
$\tan \delta$ = true dissipation factor of solid fiber
F_1, F_2 = volume fractions of solid at two different apparent densities.

The volume fraction is the ratio of the apparent density to the true solid fiber density. These expressions are accurate when the distribution of the air space is uniform in three dimensions. Unfortunately, the materials measured in this investigation are apparently not three dimensionally uniform in the distribution of air space between the fibers. The apparent dielectric constant for these materials is too high to fit in with the apparent volume fraction. The apparent dielectric constant values indicate that the fibers are stacked up in columns and that there are many narrow columns perpendicular to the electrode face which contain little solid dielectric. It was hoped to avoid this effect of apparent "pinholes" by stacking up several sheets, but this procedure apparently did not suffice. The true relation between the apparent dielectric constants at various apparent densities for these impregnated and unimpregnated papers lies somewhere between Equation 4 and a parallel capacitance arrangement.

The curves of dissipation factor for the cellulose materials by themselves indicate that the relative humidity has a pronounced effect, especially above 50% relative humidity. This effect has, in general, been known for a long time, and data have been reported by many workers in the field of dielectrics. In order to graph a wide range of dissipation factors better on the same scale, a logarithmic scale was used. At the higher frequencies the variation in dissipation factor with changing relative humidity is much less than at the lower frequencies where it may increase more than ten times on going from 15 to 98% relative humidity. The increase in the dissipation factor in the range 15 to 42% relative humidity is much less than at higher humidities; the most pronounced increase in the dissipation factor occurs from 75 to 98% relative humidity. The dielectric constant of these materials increases in the same manner, although not so great relatively as the dissipation factor. Cotton duck sems to be more seriously affected by moisture than the wood pulp papers.

The effect of adsorbed water vapor on the shape of the dissipation factor curve is interesting. Toward the lower-frequency end the moisture causes a sharp rise in dissipation factor with decreasing frequency. This lower-frequency upswing is probably associated with an increased ionic conductivity caused by the moisture. It should be remembered that the loss factor due to such conductivity diminishes as the reciprocal of the frequency.

For the unimpregnated cellulose materials, at about 10 megacycles there is a slight maximum apparent at the lower humidities, but this maximum is raised in height, broadened, and obscured by the steep rise toward lower frequencies, so that it is indistinguishable at the higher humidities. This effect was also pointed out by Yager (*10*). In dry paper and cellophane this maximum was observed by other investigators (*8*, *9*). The fact that addition of water to the cellulose seems only to raise and broaden the maximum without shifting it appears to indicate that it is associated with hydroxyl groups; but the exact role of the water, other than to increase the number of these groups, is not readily understood.

Above 25 megacycles in frequency there is a sharp rise in the dissipation factor which probably leads to another peak above 50 megacycles. This is observable in both the unimpregnated and impregnated materials, and is probably not associated with the phenolic resin.

The shapes of the curves of dissipation factor for the resin-impregnated materials are similar to those for the cellulose materials. This indicates that the resin contributes little to the shape of the curve. It does increase the series capacitance between the cellulose fibers and the electrodes, and thus raises the apparent dielectric constant. The appearance of the maximum in the dissipation factor in the impregnated alpha paper especially, and to a lesser extent in the other materials, and the generally lower dissipation factor for the impregnated materials than for the unimpregnated indicate that the resin tends to exclude the water from the cellulose so that the dielectric resembles the drier cellulose. For this reason equations for a series combination of dielectrics cannot be expected to apply, since the presence of one material affects the nature of the other.

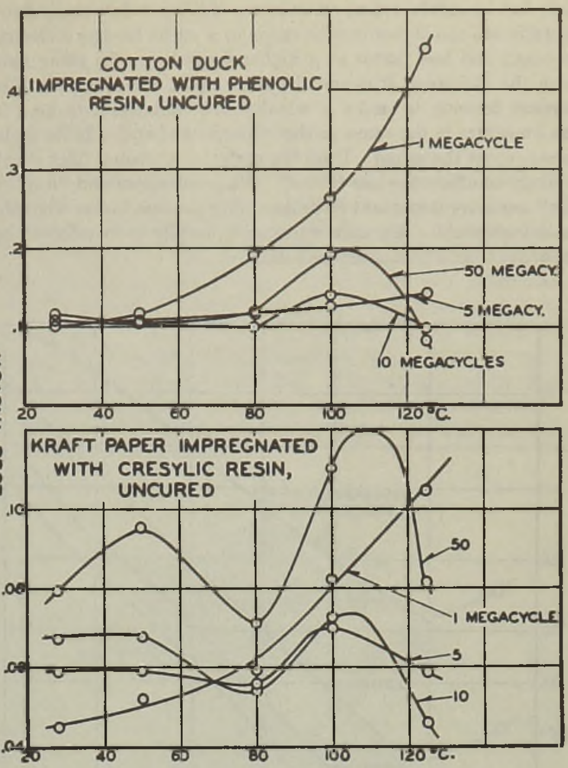


Figure 5. Loss Factors of Uncured Resin-Impregnated Materials

Figure 5 represents the loss factors for resin-impregnated cotton duck and kraft paper over a range of temperature to 125° C. These materials were conditioned at room temperature at a relative humidity of 42% previous to measurement at the higher temperatures. There appears to be a maximum loss factor at the higher frequencies in the neighborhood of 100° C. It is not known whether this is a real or apparent effect, since the attempt is made to measure a material which is not at equilibrium, with a higher-than-equilibrium moisture content. It is significant that curves of loss factor on a wood-flour-filled phenolic molding compound measured by a dynamic thermal method and reported recently have a similar shape (*7*). It is also important to note that the maximum does not appear in the one-megacycle frequency curve where, if it were due to loss of moisture or some similar effect, it might be expected to show up more prominently. There is a rise in apparent dielectric constant with increasing temperature; such a rise is caused by an internal expansion and decrease in viscosity in the material which permits molecules or parts of molecules to rotate which could not rotate at a lower temperature. It is probably caused by the resin in this case. Materials whose dipolar molecules can rotate freely at the lower temperature will have decreasing dielectric constant with increasing temperature.

PRACTICAL APPLICATIONS

This paper has presented data which, properly applied, can be useful to the engineer who is heating these materials in a high-frequency electric field. In the literature on dielectrics there are more data which, if properly interpreted, will also be useful to the engineer in the heating of other materials. There is great need for the literature on this subject to be abstracted and cataloged. Many of the data have been taken at lower frequencies; but by careful extrapolation from this lower-frequency data, an estimate can sometimes be made of a value for the dielectric constant and loss factor at a higher frequency. In using data from the literature, it cannot be emphasized too much that the hardest decision to make is whether the material measured in the literature is the same as the material at hand. Is its moisture content the same? Does the material contain a filler which is likely to affect the loss factor? Often the fillers and "impurities" are more important in determining the loss factor than the main ingredient. A porous material is usually more affected by moisture than a homogeneous solid.

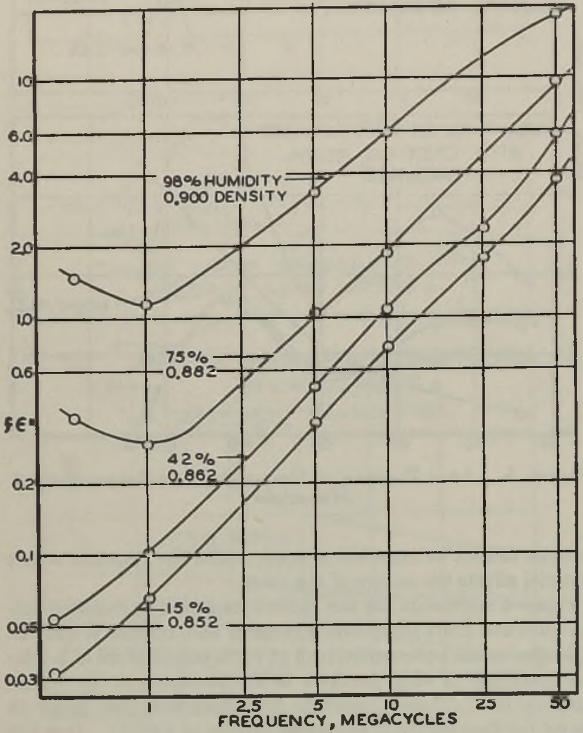


Figure 6. Heating Factor for Cotton Duck Impregnated with Phenolic Resin at 28° C.

As reported here, the data will often occur as curves of dissipation factor and dielectric constant. The heating factor is the triple product of these two and the frequency. To show how steeply the heating factor, $\epsilon''f$, rises with frequency, this quantity is plotted on a logarithmic scale for cotton duck impregnated with B-stage phenolic resin (Figure 6). The maxima in the dissipation factor curves show up here only as slight waves in the general upward trend of the heating factor curve. In calculating the heating factor for these curves, the frequency in megacycles was used, so that curves actually indicate the watts generated per cc. for 1000 volts per cm. voltage gradient in the material.

A question has been raised as to whether the dissipation factors measured at low voltages are the same at the higher voltages used in practice. At low frequencies there is observed a change with voltage of the power factor of material which contains barriers to ionic motion (i.e., heterogeneous materials). This effect should not be so important at radio frequency because the net distance of translation of the ions during a single cycle is probably much less than the separation of such barriers. The other possible effect is that the high voltage will increase the amount of ionization. Evidence in the literature indicates this is not appreciable until the voltage gradient exceeds 5,000–10,000 volts per cm. (*4*). Voltage gradients developed in radio frequency heating practice do not often exceed this range. Until further evidence to the contrary is presented, it should be assumed that the dissipation factor at these frequencies does not vary with voltage gradient for the voltage gradients up to 5,000–10,000 volts per cm.

In the application of electrodes to flat pieces which are to be heated, an air gap is often intentional or unavoidable. This reduces the radio frequency field strength in the piece and the heating, unless a constant current is kept flowing in the radio frequency leads to the electrodes. In the latter case an air gap only serves to reduce the effective capacitance and dissipation factor between the electrodes, to increase the voltage between the electrodes, and thus to leave the heating in the sample the same. The relation between the dissipation factor of such an arrangement of sample plus air gap and the dissipation factor of the sample is the same as in Equation 4. The effective dielectric constant of such an arrangement is also given in Equation 4.

It is important to the engineer in coupling his oscillator to the lead to know both the capacitance and the dissipation factor. For a given radio frequency current, the voltage between the electrodes will vary approximately as $^1/_2\ \pi fC\ (1 + \tan^2 \delta)^{1/2}$. In common practice a constant current may not be maintained. The impedance of the load which is determined by the capacitance, inductance, and dissipation factor will more directly determine the voltage by the amount of shunt impedance and "loading" they present toward the oscillator. This is illustrated by a common condition where the local circuit containing the dielectric is made to resonate. The resistance which the circuit presents then becomes $1/(2\pi fC \tan \delta)$, which expression is inversely proportional to the dissipation factor of the combination of dielectrics between the electrode. In this case the voltage between the electrodes will change almost inversely as the dissipation factor of the combination of dielectrics, and also inversely as their capacitance and the frequency. Therefore, a high voltage will result with a low dissipation factor and capacitance (or low frequency), and a lower voltage with a high dissipation factor and capacitance.

It is undesirable because of voltage breakdown to allow too large a voltage between the electrodes. Surface flashover between the electrodes on the edge of the sample may occur at about 13,000 volts per inch and may occur at the same voltage at much greater separations. The surface flashover will depend greatly upon the conditions of the surface and the electrode edges. Rounded-edge electrodes will increase the permissible voltage.

In the case where an air gap is present, voltage breakdown may occur in the air gap, since the voltage stress is greater on the air gap than the sample (Figure 7). The voltage division is given by the equation

$$V_a = V_{total} \frac{\epsilon'_s\, d_a}{d_s + \epsilon'_s\, d_a} \tag{6}$$

where V_a = voltage on air gap
d_s = thickness of sample
d_a = thickness of air gap
ϵ'_s = dielectric constant of sample

The tolerable voltages for various separations of air gaps, determined for a rather extreme electrode arrangement of rod gaps with sharp corners, were given by Berberich *et al.* (*1*). These values for breakdown voltage were determined at 60 cycles and should probably be reduced by a factor of 10–20% for high-frequency application. At radio frequency, $^1/_2$-inch separation will break down at about 9000 volts; $^1/_4$-inch separation, at 7000 volts. With porous materials breakdown within the pores of the material may occur.

When the sample is irregular in thickness, the field strength and thus the heating will be irregular unless a compensation is made. Compensation to make the field strength within the sample uniform can be made by adjusting the air gap between the sample and the electrode, making the air gap greater in the area where the sample is thinner (Figure 8). A rough rule is to keep the quantity ($\epsilon'_s d_a + d_s$) constant over the entire area of the electrodes. Metallic inserts can also be compensated for in this way. In a case where there is a laminar series of dielectrics or a uniform dispersion of one in the other, the apparent dielectric constant and dissipation factor of the combination will be approximated by the equations

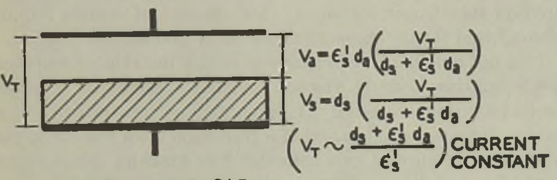
$$\tan \delta_m = \frac{F_1\, \epsilon'_2 \tan \delta_1 + F_2\, \epsilon'_1 \tan \delta_2}{F_2\, \epsilon'_1 + F_1\, \epsilon'_2}$$

$$\epsilon'_m = \frac{\epsilon'_1 \epsilon'_2}{F_1\, \epsilon'_2 + F_2\, \epsilon'_1} \tag{7}$$

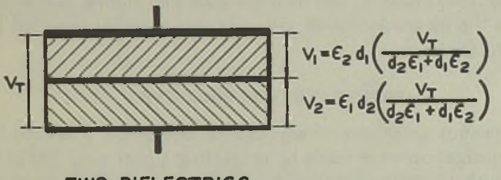
where F_1, F_2 = volume fractions of each material

These equations are valid only if the presence of one dielectric does not affect the properties of the other. The heating in each will depend upon their respective loss factors and electric field strengths in each. The field strengths may be estimated by Equation 6, replacing the value of 1 for the dielectric constant of air by the dielectric constant of the second material.

Equations 4 through 7 and those in Figures 7 and 8 are accurate only if the materials have dissipation factors less than 0.10. Most plastic materials can be considered with them. They depart from validity as the materials become quite conducting in ions. Treatment of materials which are largely conductive and less capacitative in nature, such as meat, water solutions, etc., is beyond the scope of this paper, but the equations can be simply derived if such materials are considered as resistances and their capacitance and dielectric constant are neglected. Similar equations treating materials whose capacitative and resistive impedances are of the same order of magnitude are considerably more complicated.



UNIFORM AIR GAP



TWO DIELECTRICS

Figure 7. Voltage Division between Dielectrics

For purposes of calculating the temperature rise in a material, once the field strength is known, it is necessary to know the specific heat of the material and the variation of the loss factor with temperature, if any. An average loss factor over the range of the temperature rise should be used:

$$\frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \epsilon''(T)\, dT$$

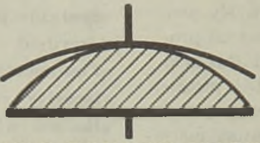
This may be obtained exactly by plotting ϵ'' as a function of temperature as in Figure 5 and taking the area under the curve to the temperature desired.

The actual temperature rise, assuming no heat loss or gain, is then given by the equation,

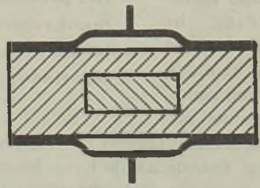
$$\Delta T = \frac{7.96 fE^2}{C\rho} \epsilon''_{av}\, \Delta t\, (\times 10^{-12})^\circ \text{ C.} \tag{8}$$

where C = specific heat, calorie/gram
ρ = density
Δt = time of voltage application

Unfortunately other factors affect the temperature rise, such as heat diffusion to the surface (*3*), where it is lost by radiation or convection, and heat loss due to vaporization of volatile material within the pores which diffuses out. The latter may really be considered as part of the former. There is also heat generation within the material by chemical reaction, which is accelerated by temperature rise. For example, in practical heating of phenolic laminates the temperature has been noted to rise after the radio frequency voltage has been removed. The variation in loss factor discussed previously may be due in part to a chemical reaction in the resin which hardens it at the higher temperatures or to loss of a volatile constituent.



VARIABLE THICKNESS DIELECTRIC
$\epsilon'_s d_a + d_s$ = CONSTANT



METAL INSERT
$\epsilon'_s d_a + d_s$ = CONSTANT

Figure 8. Diagram for Compensation to Make Field Strength Uniform within Sample

All these phenomena make the accurate calculation of temperature rise a difficult dynamic problem, although in many cases approximations can be made. For example, with a short heating cycle the variation in loss factor due to chemical reaction may be neglected, since the chemical reaction does not proceed appreciably until the radio frequency heating is nearly over. Considerably more data are needed, however, on the quantity of heat generation from the heat of reaction and loss of volatile constituents for various molding materials.

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VISCOSITY PATTERNS OF PEANUT PROTEIN SOLUTIONS

Comparison with Other Vegetable Proteins and with Casein

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Methods for preparing and determining the viscosity of vegetable protein solutions at useful concentrations are described. Data are presented which show the influence of concentration, heat, pH, time, and other factors on the viscosity relations of peanut protein solutions made alkaline with sodium hydroxide. These factors are, in turn, influenced by the conditions under which the peanut meal is prepared, by the methods employed in separating the protein from the meal, and by the subsequent treatment received by the separated protein. The viscosity behavior of peanut protein solutions is compared with that of solutions of casein and of soybean and cottonseed proteins.

VEGETABLE proteins are comparatively new in the field of industrial proteins. In the past this field has been dominated principally by casein, gelatin, and the less pure gelatins marketed as bone and hide glues.

Chemical methods have generally been found inadequate for following the changes which have taken place in processing or modifying these older, well established proteins of animal origin, or in evaluating their suitability for any given purpose. For this reason physical measurements have been more often employed; of these measurements, the determination of the viscosity of protein solutions has been of major importance.

A knowledge of the influence of concentration, heat, pH, time, and other factors on the viscosity relations of vegetable protein solutions is essential for the rational industrial utilization of these proteins. In the case of proteins from oilseed meals, the effects of these factors are in turn influenced by the conditions under which the meal was prepared and under which the protein was separated from the meal. However, to our knowledge, no systematic investigation of these relations has been reported.

In connection with the work on the utilization of peanut proteins in the production of adhesives, fibers, sizes, etc., at this Laboratory, it was found that the viscosity of the protein solutions was of paramount importance in evaluating the protein and in controlling the products and processes under investigation.

While the results presented here are concerned primarily with peanut protein, these data are compared with those obtained with soybean protein, cottonseed protein, and casein. A comparison of solutions of peanut protein with those of soybean protein is of special interest because soybean protein is at present the only commercially available vegetable protein which is soluble over a wide pH range. Zein, the only other vegetable protein of industrial importance, is not soluble in aqueous solutions below pH 11.5 (*10, 12*). Comparison of peanut protein with casein is of interest because solutions of casein are used industrially over a wide pH range and resemble solutions of peanut protein in that their viscosities are affected by pH. Viscosity data for solutions of cottonseed protein are also included because cottonseed represents an economically important commodity of the South.

CHOICE OF VISCOMETER

The Hoeppler viscometer, which employs the rolling ball principle, was selected because past experience indicated that this instrument was best suited for the purpose. The advantages of this type for measuring concentrated protein solutions are: The instrument can be used over an extremely wide viscosity range; readings can be made rapidly and are convertible to absolute viscosity units; test solutions can be kept in the instrument for long periods without "skin" formation or loss of water by evaporation; readings can be repeated as often as desired without requiring replacement or transfer of the sample; apparent gel viscosity as well as sol viscosity can be measured on thixotropic solutions; the amount of sample required is small; and the instrument can be easily and rapidly cleaned.

It is not possible to determine with this instrument whether a given solution is truly viscous. Visual observation of peanut protein solutions, especially at high protein concentrations and pH values, gives some indication of a transition from viscous to plastic flow. Because of this behavior flow-pressure measurements would be useful in further investigating the rheological properties of peanut protein solutions. Hoeppler (*7*) discussed the theoretical aspects of the instrument which bears his name, and a general study of the inclined tube and rolling ball as applied to the measurement of viscosity was recently reported by Hubbard (*8*).

PREPARATION OF PROTEINS

The peanut proteins and soybean protein (SB3) prepared for this investigation were made by extracting 1 part meal (20 to 40 mesh) with 10 parts of water at 25° C. and at the pH shown in Table I. The meal was separated from the liquor by means of a solid basket centrifuge. After the centrifugate was allowed to settle for about 2 hours, it was clarified by filtration. The protein was then precipitated (25° C.) from the filtrate at approximately the isoelectric point by means of sulfur dioxide. The pH of precipitation is also shown in Table I. After settling overnight, the protein curds were filtered and dried at 50° C. (An approximate estimate of the solubility of these proteins in concentrated solution is also recorded in Figure 1 and will be explained later.)

It should be pointed out that when proteins were prepared by extracting the meal at a pH above 7.5, the meal slurry was adjusted to approximately pH 7.5 with sulfur dioxide after 2 hours of alkaline digestion. Preliminary experiments indicated that the time of digestion at the higher pH greatly influences the viscosity characteristics of the recovered protein. In order to evaluate the influence of pH, it is therefore necessary to digest for a uniform period of time.

Table I. Preparation and Solubility Characteristics of Proteins

Protein No.	Preparation Conditions			Highest pH at Which Solubility is:	
	Meal used	pH of extn. (NaOH)	pH of pptn. (SO_2)	Poor	Fair
P1	Peanut, solvent-extd.	7.39	4.50	7.6	9.4
P1-L				7.5	9.2
P2		9.92[a]	4.55	9.95	10.5
P2-L				8.6	10.2
P3		11.10[a]	4.40	9.2	10.8
P3-L				8.8	9.8
P4-L	Peanut, hydraulic-pressed	9.88[a]	4.70	8.2	9.9
P5-L		10.00[a]	4.40	7.5	9.4
P6-L		10.00[a]	4.40	7.5	9.5
P7	Peanut, solvent-extd.	7.30[b]	4.30[d]	9.5	10.3
SB3	Soybean, solvent-extd.	7.60	4.54	6.6	9.5
CSA-L CSH-L	Cottonseed, solvent-extd.	7.00[c]	4.0[e]	11.7	12.6
SB1	Soybean, solvent-extd. (?)	Unknown	(SO_2 present)	8.0	9.6
SB1-L				7.5	8.9
SB2		Unknown	(SO_2 present)	8.0	8.9
C	Casein	...	(Lactic acid)	...	7.5

[a] pH of meal slurry reduced to approximately 7.5 with SO_2 after 2-hour digestion.

[b] pH adjustment made with Na_2SO_3 instead of NaOH.

[c] 0.5 *M* NaCl used with NaOH as a solvent.

[d] Protein curd re-dissolved and digested at pH 11.2 for 2 hours and reprecipitated at pH 4.4.

[e] Diluted at this pH with 4 volumes of water.

Considerable variation was found to exist in the apparent density of the dry isolated proteins; some were hard and flinty while others were porous and friable. Since, in preparing solutions for viscosity measurement, the rate of solution of the protein obviously depends upon the rate with which the solvent penetrates the protein particle, it was found necessary to prepare protein samples of uniformly small particle size in order to obtain reproducible results, especially in the lower pH ranges where the solubility of the protein is incomplete. Uniformly powdered samples were obtained by grinding the proteins in a Raymond laboratory mill. Precautions were taken to keep the mill cool in order to avoid overheating the protein. Sieve analysis showed that about 97% of the ground proteins passed a 60-mesh sieve and 80% or more passed a 100-mesh sieve.

Dry protein samples which were leached to remove soluble nonprotein material have an "L" following their number. Leaching was accomplished by mixing the ground protein with about 5 parts of cold distilled water, allowing the protein to settle, and siphoning off the supernatant liquor. These operations were repeated five times, after which the protein was redried at 50° C. The supernatant liquor was always found to attain a pH within the isoelectric range of the protein. Therefore, no solution of protein could have taken place during leaching.

PREPARATION OF PROTEIN SOLUTIONS

Throughout this paper the term "solution" refers to any preparation made by dispersing or dissolving proteins in an aqueous medium. The concentrations of protein in the solutions prepared for viscosity measurement were selected after preliminary trials had indicated the range of concentration which would yield solutions with flow characteristics within, or reasonably near, the commercially useful range. The use of concentrated protein solutions for investigations of this nature is important because often the reported results of viscosity measurements on solutions of low protein concentration are misleading when extrapolated to higher and more useful concentrations. Sodium hydroxide was the alkali used to prepare all of the solutions.

Sufficient dry protein, adjusted to a 7% moisture basis, is used so that the 50 grams of solution finally obtained will have the desired protein concentration. The weighed protein sample is added to a previously tared mixing unit consisting of a 50-ml. beaker and stirrer. An Aero-Mix air-driven stirrer, having a stainless steel shaft and propeller which can be quickly and easily removed from the turbine and kept in the protein solution until preparation of the solution is completed, was found to be best suited for this purpose. The weight of alkali solution (0.0125 gram of sodium hydroxide per ml.) required to bring the final protein solution to the desired pH value is estimated, and water at 25° C. is added slowly to the dry protein until the weight of the contents of the beaker is 49.5 grams minus the estimated weight of alkali solution to be added later. The water should be added in small portions and the mass stirred to a smooth paste to ensure wetting of the protein particles.

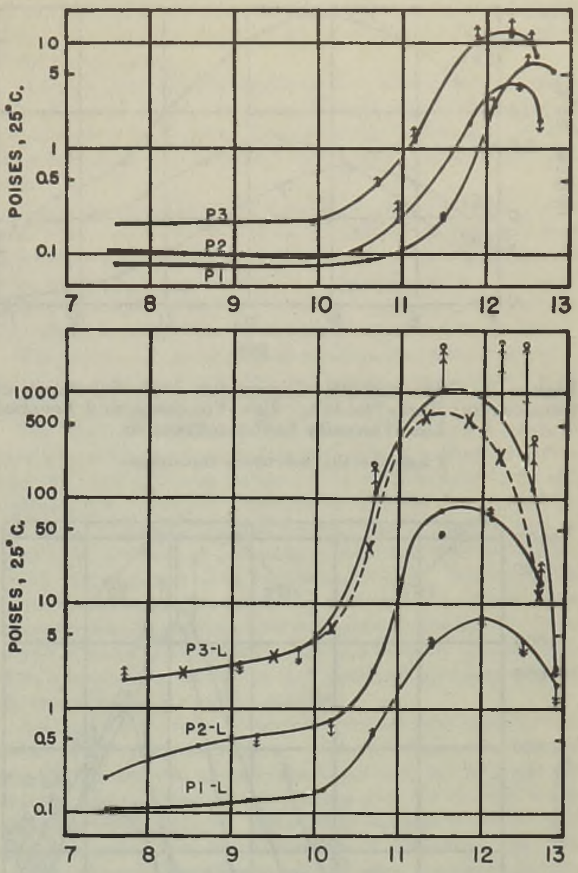

Figure 1. Effects of pH of Extraction and of Removing Soluble Nonprotein Material on Viscosity of 18% Solutions of Peanut Proteins P1, P2, and P3, Extracted for 2 Hours at Approximately pH 7.5, 10.0, and 11.0, Respectively

Curve X—X represents viscosity of protein P3-L on same nitrogen basis as P3. Solution gelled overnight ○.

Two or three drops of octyl alcohol are added as a defoaming agent, and the beaker is placed in a shallow water bath maintained at the desired temperature. The stirrer is attached to the turbine and stirring is continued until the contents of the beaker attain the temperature of the bath. The required amount of alkali solution (previously estimated) is added slowly with stirring, and the mixture is stirred continuously for exactly 30 minutes after the addition of alkali is complete. Constant speed of stirring would probably be advantageous, but this appears impractical in working with solutions over a wide range in viscosity.

The beaker containing the protein solution and stirrer is then removed from the water bath and placed in a constant-temperature bath at 25° C. in order to cool solutions prepared at higher temperatures and to maintain the temperature of solutions prepared at 25° C. The beaker is removed from the water bath in time to permit the addition of sufficient water at 25° C. to bring

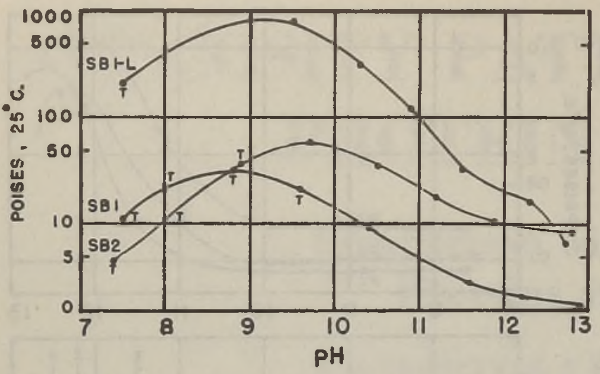

Figure 2. Viscosity-pH Curves for 18% Solutions of Commercial High-Viscosity, Low-Viscosity, and Leached Low-Viscosity Soybean Proteins

T indicates that solution is thixotropic.

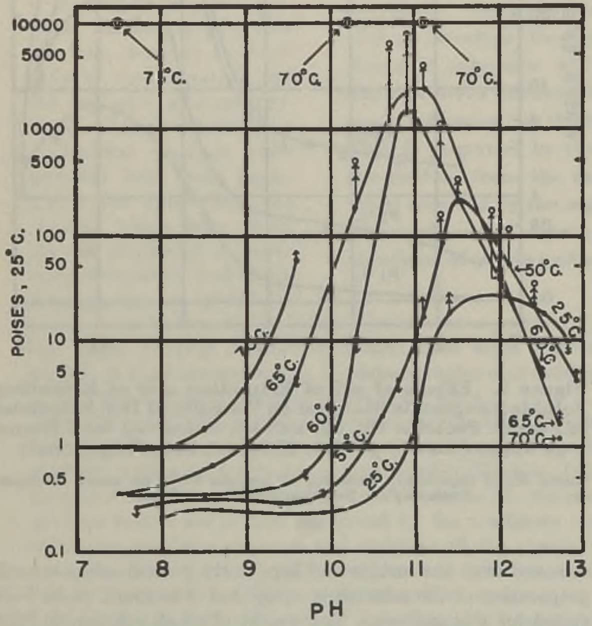

Figure 3. Viscosity-pH Curves for 20% Solutions of Protein P1-L after Heating for 30 Minutes at Various Temperatures

Solution gelled: overnight ○, during preparation ⊙.

the total weight of the protein solution to 50.0 grams, to transfer the solution, and to add the proper balls to the viscometer so that the first viscosity reading can be made at exactly one hour after the addition of the alkali. Five minutes are ordinarily allowed for these operations.

MEASUREMENT OF VISCOSITY

The protein solution is poured into the viscometer (temperature of the water jacket, 25° C.) and a viscosity measurement is made. Measurement is repeated until satisfactory duplication of readings is obtained. Viscometer balls should be chosen so that the minimum period of fall recommended for the instrument is obtained.

After the initial viscosity value has been determined, the solution is allowed to remain in the viscometer and additional measurements are made as desired at any time interval thereafter. Since concentrated vegetable protein solutions must have a reasonably long "working life" when used industrially, the solutions in these experiments were held in the viscometer for 2 hours and duplicate readings were made at 1- and 2-hour intervals after the initial reading to determine the extent of change in viscosity of the solution with time.

The use of the term "viscosity patterns" in the title can be appreciated when consideration is given to the fact that it is not unusual for vegetable protein solutions to increase five- to tenfold in viscosity during the 2–3 hours following the addition of alkali. Consequently, even with careful timing, the average of viscosity measurements made on replicate solutions may vary ±20% from the mean in cases where the viscosity of the solution is changing rapidly.

In the case of solutions having more stable viscosities, variations from the mean seldom exceed ±10%. Such variation is of no practical significance and does not appreciably alter the shape of the viscosity curves. Viscosity determinations were made on duplicate solutions at the start of the investigation to establish the limitations of the method. Thereafter, duplicate solutions were made up only when a viscosity reading appeared to be erratic.

Thixotropic behavior will not ordinarily become apparent until the protein solution has been held for a while in the viscometer without agitation. Evidence of thixotropy is indicated if the second of duplicate readings on the same solution is lower than the first. In such cases the true viscosity of the sol can be obtained by moving the viscometer ball through the solution several times to break up the gel which is temporarily formed. Under these conditions the sol viscosity may be observed when the time of fall of the viscometer ball becomes constant. If the measurement of gel viscosity as well as sol viscosity is required, the viscometer balls should be placed and held at the top of the viscometer tube in position for measurement so that no gel breakdown will be caused by adjusting the position of the balls immediately before measurement.

After the initial viscosity reading has been made, the protein solution remaining in the beaker is examined microscopically for solubility of the protein; the pH of the solution is determined in a Beckman pH meter (Model G) equipped with a glass electrode designed for the pH range 9 to 14. In microscopic examination at a magnification of 100 diameters, the presence of many large, swollen, protein particles is arbitrarily taken to indicate poor protein solubility (Table I). Solubility is considered complete if visible particles are absent and the solution is clear and homogeneous. Solubility is considered fair if only a few swollen particles are visible and the solution does not appear to be clear or homogeneous.

When the viscosity measurements are completed, the protein solution is returned to the beaker and the solution is allowed to stand overnight at room temperature (approximately 25° C.). The solution is examined the next morning for gelation.

The viscosity data are presented graphically in Figures 1 to 7. All viscosities were determined at 25° C. and, except where otherwise noted (Figures 3 and 7), all protein solutions were prepared at 25°. The arrows on the curves indicate the change in viscosity at hourly intervals. The absence of arrows at a point on any of the curves (with the exception of the curves in Figure 2) means that no change in viscosity occurred during the 2-hour period of observation. The presence of only one arrow at a point usually indicates that no change in viscosity occurred after the first hour in the viscometer, although in some instances the viscosity was found to be constant during the first hour but to have undergone a change during the second hour.

EFFECTS OF SOLUBLE NONPROTEIN MATERIAL

The proteins used in preparing solutions designated P1, P2, and P3 (viscosity curves shown in the upper portion of Figure 1) were separated from solvent-extracted peanut meal, and no special care was taken to wash the precipitated protein curds before they were dried. The lower portion of Figure 1 shows the viscosity curves for solutions of these same proteins after the dried proteins had been leached several times with water to remove soluble nonprotein material and then redried. The effect of leaching on the viscosity of the protein solution is most marked in the case of the protein extracted at pH 11.0 (P3). The magnitude of this effect is illustrated by comparison of the curves for preparations P3 and P3-L. The maximum viscosity shown in the former was 10 poises and that in the latter, 1000 poises. Removal of the soluble, nonprotein material also raised the nitrogen content of the protein (P3) from 16.06 to 16.55% (P3-L). If the viscosity curve for P3-L is redetermined on the same nitrogen basis as protein P3, the curve obtained (broken line below the curve for P3-L, Figure 1) indicates that the increase in viscosity is due primarily to the removal of soluble nonprotein material. In the case of protein P2, extracted at pH 10.0, the increase in viscosity on leaching was much less than that found for protein P3. With protein P1, extracted at pH 7.5, the effect of leaching on the viscosity of the solution was negligible. These differences in the changes in viscosity brought about by leaching of the proteins are probably due to differences in the salt content of the unleached proteins. The salt content varies because more alkali is used to extract the protein at the higher pH values, and this alkali is subsequently neutralized to give corresponding amounts of salts when the protein is precipitated by acid.

The effect of the presence of salts on the viscosity of peanut protein solutions differs from that reported for casein solutions. Sutermeister and Browne (*11*) state: "In general the higher the content of ash in the casein, the higher the viscosity of its solutions." Whether the use of alkalies and acids other than sodium hydroxide and sulfurous acid to separate peanut protein from the meal will leave salts in the dry protein that have a different effect on the viscosity of its solutions, has not been investigated. However, the use of sulfurous acid for the precipitation of vegetable protein in large-scale industrial operations is preferred because this acid is relatively cheap and prevents bacterial decomposition of the protein-curds.

Not only must bacterial action be controlled during precipitation of the curd, but it must also be controlled during extraction of vegetable proteins in plant-scale operations; and sodium sulfite is often used alone or in conjunction with other alkalies for this purpose.

There is a possibility that soluble nonprotein material, other than salts, may be present in the unleached proteins, and that appreciable amounts of this material are extracted from the meal when the extraction is carried out at high pH values. The presence of such material and of protein decomposition products may also affect the viscosity of solutions made from these proteins.

The viscosity of peanut protein solutions increases as the pH at which the protein is extracted is increased, as is evident from curves in the lower portion of Figure 1.

The effect of leaching on the viscosity of solutions prepared from commercial soybean protein is illustrated in Figure 2. Proteins SB1 and SB2 were labeled by the manufacturer "low- and high-viscosity protein", respectively. The effectiveness of removing the soluble nonprotein material from soybean protein in raising the viscosity of the subsequent protein solution is illustrated by comparison of curves SB1 and SB1-L. While only the initial viscosities (1 hour after the addition of the alkali) were determined on the solutions used in the series represented by these curves, it should be pointed out that the viscosity of these solutions was relatively stable and that leaching the soybean protein did not appreciably alter the stability.

Leaching and redrying of vegetable proteins during their manufacture is, of course, impractical. However, the removal of salts and other nonprotein material was found to be necessary for the evaluation of the effect of their presence upon the viscosity of the various protein solutions. It is obvious also that the presence of salts masks the effect on the viscosity of the protein solutions brought about by variation in pH and other processing factors. A practical procedure for the commercial production of vegetable

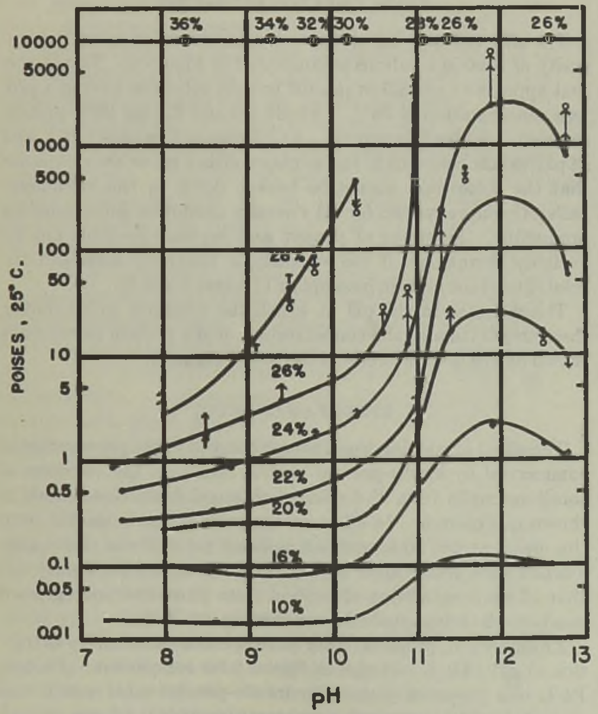

Figure 4. Effect of Protein Concentration on Viscosity–pH Curves of Solutions of Protein P1-L

Solution gelled: overnight ⊙, during preparation ⊙. T indicates solution is thixotropic.

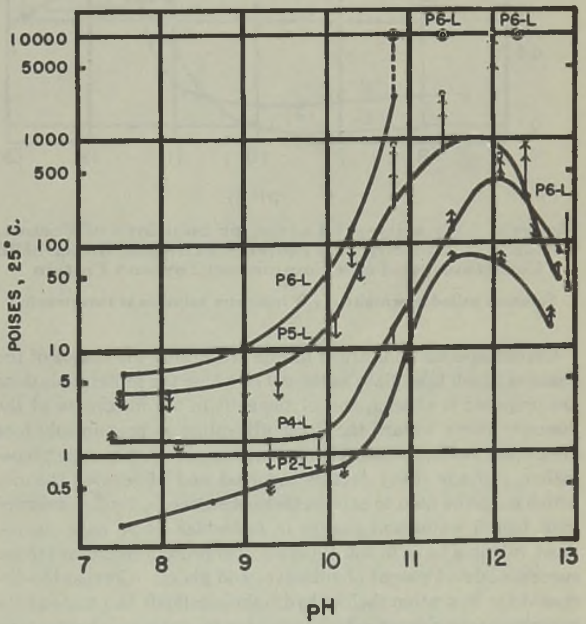

Figure 5. Viscosity–pH Curves for 18% Solutions of Proteins Extracted at pH 10.0 from Hydraulic-Pressed Peanut Meals and Protein Extracted from Solvent-Extracted Meal under the Same Conditions (P2-L)

Solution gelled: overnight ⊙, during preparation ⊙, in viscometer ⊕.

proteins of relatively uniform quality entails the reduction of the content of nonprotein material by re-solution, re-precipitation, and thorough washing of the protein curds. Such a procedure is probably standard practice with some manufacturers.

EFFECT OF TEMPERATURE

The changes in viscosity which result when 20% solutions of peanut protein are subjected to various temperatures for 30 minutes before measurement are shown in Figure 3 for protein P1-L, selected for this series of experiments and for the series which follows (Figure 4). This protein was prepared under conditions that would be expected to produce a good yield and minimum protein denaturation (*3*).

In the region of maximum viscosity the effect of heat becomes significant at 50° C. and above. In the lower pH range heating the solution has little effect until 65° C. is reached. At 75° C., however, the viscosity increases so rapidly that gelation takes place while the solutions are being prepared, even at the lowest pH values. The placing of the double circles (⊙) on the 10,000-poise ordinate in Figures 3 and 4 is for convenience. Stable gelled solutions do not exhibit viscous flow properties. The viscosity of the solutions has a tendency to become less stable near the maximum of the curves as the temperature at which the solutions are prepared is increased.

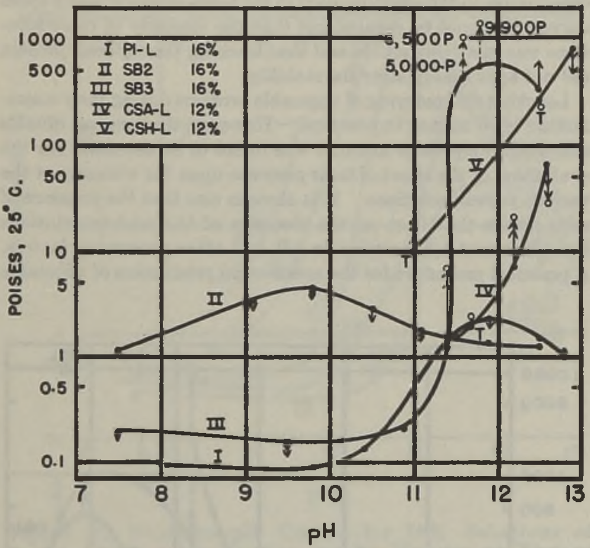

Figure 6. Viscosity–pH Curves for Solutions of Peanut, Cottonseed, and Soybean Proteins Extracted under Mild Conditions, and of a Commercial Soybean Protein

Solution gelled overnight ○; T indicates solution is thixotropic.

Certain speculations are of interest regarding the causes of the changes which take place as the pH at which the protein solutions are prepared is altered, and of the shift in the maximum of the viscosity curve toward the lower pH values as protein solutions are heated at successively higher temperatures during their preparation. Of the many factors involved and of several theories which might be used to explain these phenomena, those concerned with bound water and change in molecular shape have proved most valuable to us in the application of protein solutions for the successful development of adhesives and fibers. Gortner (*5*) discussed the hydration shell of hydrophilic colloids and some of the experimental evidence which indicates that the water molecules in this hydration shell differ from the state which characterizes water molecules in ordinary liquid water. Gortner also pointed out the effect of this solvation process on the parabolic relation between viscosity and concentration in lyophilic systems (*6*). When this theory is applied to the interpretation of viscosity data on vegetable protein solutions, it appears possible that, up to the point of maximum viscosity, an increase in pH causes the protein molecules to bind more water and thus remove water which would otherwise be available as solvent. This, in effect, increases the actual concentration of protein in the remaining free water and may thus account for the rapid increase in viscosity.

With increase in pH beyond the point of maximum viscosity, the effect of pH on the amount of water bound by the protein molecules appears to be reversed; but another factor must also be considered. As the pH of a protein solution is increased, a point is reached where considerable degradation of the protein molecules begins to take place. At pH values beyond the point of maximum viscosity, this effect of protein degradation may be sufficiently great to predominate over the effect of a possible increased capacity of the protein molecule to bind water, or it may simply accompany and augment a reversal in the tendency of the protein to bind water. As the temperature at which the protein solutions are prepared is raised, the rate of protein degradation increases and consequently causes the viscosity maximum to shift toward lower pH values.

The effect of temperature on the rate of protein degradation can also be observed in the viscosity of solutions prepared at the highest pH values where the shift in the viscosity curves is toward lower pH with increase in temperature.

Another possible explanation of the viscosity behavior of vegetable protein solutions merits consideration. It has been reported that globular proteins upon acidification or alkalization are transformed irreversibly into molecules of the micellar type (*1*). If such a change in molecular shape actually takes place in the case of the globular vegetable proteins when they are dissolved at various pH's and temperatures, it would be expected that the viscosities of the protein solutions would be affected. This effect of molecular shape on viscosity was recently reviewed by Lauffer (*9*).

EFFECT OF CONCENTRATION

The effect of varying the protein concentration upon the viscosity of protein solutions is illustrated in Figure 4. Thixotropy first appears at pH 8.5 in peanut protein solutions having a protein concentration of 26%. At pH 9.0 and 9.5 the 28% protein solutions are also thixotropic. At concentrations above 28% and at pH values below 10.0, the solutions either gel or are so viscous that the thixotropy cannot be broken down by the viscometer balls; therefore, values for sol viscosity cannot be determined reproducibly. Solutions of peanut and soybean proteins are invariably thixotropic if the viscosity is relatively high and the solubility of the protein incomplete (Figures 2 and 4).

The decrease in the pH at which the solutions gelled during their preparation as the concentration of the protein increased is shown by the double circles at the top of Figure 4.

EFFECT OF COOKING

The effect of cooking conditions employed in the preparation of commercial hydraulic-pressed peanut meals on the viscosity of solutions made from the protein obtained from these meals is shown in Figure 5. In all cases the protein was extracted from the meals at pH 10.0, and the isolated protein was thoroughly leached with water after drying. It was shown previously (*2*) that efficient extraction of protein from most hydraulic-pressed meals can be accomplished by extracting at pH 10.0.

Protein P2-L, prepared from solvent-extracted meal by extraction at pH 10.0, is included in Figure 5 for comparison. Protein P4-L was prepared from a hydraulic-pressed meal which was cooked for 76 minutes at a temperature which did not exceed 215° F. Protein P6-L was prepared from a press meal which was cooked for one hour at a temperature which increased from approximately 175° F. in the first stack of the cooker to approximately 230° in the final stack; at no time did the temperature exceed 240° F. The cooking conditions employed in processing the meal from which protein P5-L was prepared are unknown, but the low peptizability of the nitrogen in this meal would indicate that it had been subjected to severe cooking treatment (*2*, *3*, *4*).

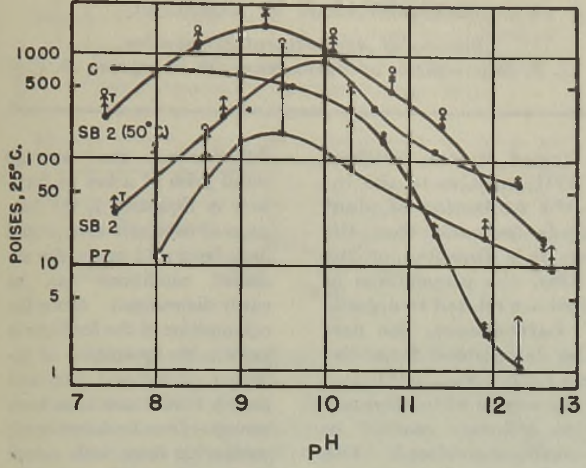

Figure 7. Viscosity–pH Curves for 20% Solutions of Lactic Acid Casein C, a Commercial High-Viscosity Soybean Protein SB2 (Heated and Unheated), and a Peanut Protein P7 (Prepared to Resemble the Casein and Soybean Proteins)

Solution gelled overnight ○.

It is apparent that, when peanut meal is moderately cooked, solutions of the proteins isolated from it possess higher viscosities than do solutions of the protein isolated from uncooked meal. However, when meals are subjected to severe cooking conditions, the ability of the protein isolated from these meals to form solutions of high viscosity is diminished. Proteins prepared from hydraulic-pressed meals appear to yield solutions in the lower pH range which become considerably less viscous on standing.

Figure 6 compares the viscosities of solutions of a commercial soybean protein and of specially prepared peanut, soybean, and cottonseed proteins. When the pH–viscosity curves for solutions of soybean protein prepared in the laboratory from solvent-extracted meal under mild conditions (curve III) and of a commercial soybean protein (curve II) are compared, it is evident that the commercial protein has been modified so that solutions having relatively stable viscosities over the complete alkaline pH range can be prepared from it. Solutions of the soybean protein prepared under mild conditions (curve III) were so markedly unstable at pH 11.5 to 12.0 that concentrations above 16% gelled during preparation. A pH–viscosity curve for a 16% solution of a peanut protein, which had also been prepared from solvent-extracted meal under mild conditions, is included (curve I) for comparison.

If a peanut protein curd is divided, one portion is dried at 50° C., and another is dried at room temperature, solutions prepared from the two will give identical pH–viscosity curves. This is also true for soybean protein. However, in the case of cottonseed protein (Figure 6, curves IV and V), there is considerable difference between the viscosities of solutions of the air-dried protein (CSA-L) and solutions of the protein dried at 50° C. (CSH-L). Cottonseed protein is not completely soluble at any of the pH values investigated, and the curves extend only over a very narrow pH range. Likewise, it was found necessary to limit the protein concentration of these solutions to 12% to prevent gelling. Because of the low solubility of cottonseed protein, it is difficult to obtain reproducible viscosity measurements. Consequently, the curves given for solutions of cottonseed protein must be considered only roughly indicative of the magnitude of the viscosity relations.

Figure 7 compares the viscosities of solutions of a commercial soybean protein (SB2) and of a specially prepared peanut protein (P7) with those of solutions of a commercial lactic-acid-precipitated casein (C). It is apparent that the commercial soybean protein has been modified to change its viscosity characteristics. Because of this modification, it is more like casein in viscosity characteristics than unmodified soybean protein.

An attempt was made to modify the viscosity characteristics of peanut protein with the result shown in curve P7. A protein curd was redissolved and digested at pH 11.2 for 2 hours. The original curd was obtained by extracting peanut meal at pH 7.3 and precipitating the protein at pH 4.3. All of the factors involved in obtaining this modification have not yet been fully determined.

In this connection it should be pointed out that extracting peanut protein from meal at pH 11.0 for 2 hours (P3-L, Figure 1) does not affect the shape of the viscosity curve appreciably, whereas digesting the separated protein at the same pH in the curd stage changes its shape materially. It is of interest also to note the extremely unstable viscosity exhibited by solutions of protein P7 as compared with those by other peanut proteins investigated and by commercial soybean protein SB2. Solutions of protein P7 gelled when heated at 50° C., whereas solutions of the soybean protein remained as sols and gave the curve shown in Figure 7 (SB2 at 50° C.). It is of interest to compare the effect of heating solutions of commercial soybean protein at 50° C. (Figure 7) with that of similar treatment on peanut protein (Figure 3).

The solubility data in Table I show only rough qualitative differences because the improvement in solubility with increase in pH is gradual. None of the vegetable proteins investigated is so soluble as casein except at the higher pH values. Where it is possible to compare the solubility of leached and unleached peanut and soybean proteins, there appears to be a tendency for the leached to be slightly more soluble. Comparison of the solubility of peanut proteins extracted or digested at the higher pH values (P2, P2-L, P3, P3-L, and P7) with those extracted at pH 7.5 (P1, P1-L), reveals that treatment of the meal or protein with alkali at high pH values lowers the solubility of the protein. Proteins from the hydraulic-pressed meals investigated (P4-L, P5-L, P6-L) are as soluble as, if not more so than, protein extracted from solvent-extracted meal at the same pH (P2-L).

Moderate heating of the solutions during preparation was found to have little influence on solubility. The solutions prepared at the lower pH values were somewhat "smoother" at the higher temperatures, which indicated that the larger swollen particles were more disintegrated than in solutions prepared at room temperature.

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Price Factors in Plant-Food Consumption

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An analysis is presented of United States fertilizer statistics for the years 1925 to 1941, relative to the influence of plant-food prices on the utilization of plant food in agriculture. The analysis indicates that the percentage nitrogen in fertilizers is a function of the ratio, $N_{price}/(P_2O_5 + K_2O)_{price}$. Also, the proportions of organic and chemical nitrogen used are related to organic and chemical nitrogen prices. Furthermore, the percentage P_2O_5 in fertilizers can be determined from the nitrogen percentage and the ratio, $N_{price}/(P_2O_5)_{price}$. The relations presented describe the way in which farmers and the fertilizer manufacturing industry reacted to changes in prices during the period considered. The estimates of the prospective reaction to other changes in prices assume that this behavior pattern continues in the future as it has been during the past. To the extent that new conditions modified the present behavior patterns, the actual behavior may differ somewhat from that estimated on the basis of this past experience.

AMERICAN farmers and the fertilizer and nitrogen industries are interested in the problems associated with the utilization of the Nation's expanded synthetic ammonia fixed-nitrogen capacity. Three questions usually arise in a discussion of the subject. First, what is the probable postwar price of fertilizer nitrogen? Second, how much fertilizer nitrogen will farmers use after the war? And third, how will the expected reduced price of nitrogen affect the use of phosphoric acid and potash? It is not the purpose of this paper to give specific answers to these questions, but certain relations between plant-food prices and consumption will be presented.

Two general principles are now well established and these will be used in this paper without further discussion:

1. Farmers in the United States spend a definite percentage of income for fertilizers, regardless of plant-food prices (*1*). Hence, with income constant, as the retail prices of fertilizers fall, the quantities purchased rise in inverse proportion. The fertilizer tonnage purchased by farmers in any year may be determined by Equation 1:

$$\text{Fertilizer tonnage} = \frac{k\ (\text{farm income in dollars})}{\text{av. retail price per ton in dollars}} \qquad (1)$$

The value of k depends upon the particular expression of farm income used. According to Mehring and Shaw, if previous year's total cash income is used, $k = 0.0268 \pm 0.0004$.

2. The retail price of a ton of fertilizer in any year tends to be the wholesale cost of the plant food contained plus a uniform amount per ton to cover the cost of transportation, processing, and distribution (*3*). For example, the difference in retail price between a ton of 2-12-6 and a ton of 3-18-9 in any year is nearly equal to the wholesale cost of one unit of nitrogen, six units of phosphoric acid, and three units of potash. Thus, any change in the wholesale price of nitrogen, phosphoric acid, or potash will be wholly reflected in the retail price of a ton of fertilizer.

Proceeding from the above principles, the problem of determining the influence of wholesale prices of nitrogen, phosphoric acid, and potash on the consumption of these materials in fertilizers is resolved into finding the effect of wholesale prices on the average analysis and total plant-food content of fertilizers. If the composition and total plant-food content of fertilizers are known, the cost of the materials in the average ton of fertilizer can be determined for any assumed set of prices. This cost, added to the average processing and distribution cost per ton found for a given year, will give the average retail price of a ton of fertilizer that would have prevailed in that year under the assumed prices. Substituting the average retail price of a ton of fertilizer in Equation 1, the tonnage of fertilizers that would have been sold under the assumed conditions can be easily determined. Since the composition of the fertilizer is known, the quantities of nitrogen, phosphoric acid, and potash that would have been consumed can be determined; comparing these with actual consumption in that year, the influence of given price changes on consumption will be apparent.

Four relations must be established; the influence of wholesale prices of plant food on the total plant-food content of fertilizers, the influence of prices on the percentage of nitrogen in fertilizers, the influence of prices on the percentage of phosphoric acid in fertilizers, and the influence of prices on the percentage of potash in fertilizers. It is obvious that these four relations are not independent. The determination of any three establishes the fourth. The first three will be examined, and finally the effect of certain assumed price changes will be evaluated. First, however, the data on which the developments are made will be examined.

WHOLESALE AND RETAIL PRICES

Wholesale prices of fertilizer materials for the years 1925 to 1941 are given in Table I. Interpretations based on this table are subject to the limitations of the data. An average price for a

TABLE I. WHOLESALE PRICES OF FERTILIZER MATERIALS PER UNIT

Year	Chem. N[a]	Organic N[a]	P_2O_5 as Superphosphate[b]	K_2O as Muriate[b]	All Plant Food[c]	All N[c]	P_2O_5 + K_2O[c]
1925	$2.77	$4.48	$0.60	$0.58	$1.18	$3.19	$0.593
1926	2.60	4.62	0.60	0.60	1.15	3.06	0.600
1927	2.47	5.13	0.54	0.65	1.15	3.07	0.571
1928	2.41	6.05	0.58	0.67	1.18	3.02	0.606
1929	2.18	5.00	0.61	0.67	1.10	2.62	0.628
1930	2.00	4.48	0.54	0.68	1.03	2.38	0.582
1931	1.72	2.84	0.49	0.68	0.90	1.94	0.548
1932	1.27	1.64	0.46	0.68	0.75	1.36	0.530
1933	1.25	2.43	0.43	0.66	0.76	1.47	0.504
1934	1.30	3.08	0.49	0.49	0.79	1.69	0.490
1935	1.25	3.32	0.49	0.42	0.76	1.60	0.466
1936	1.30	3.66	0.48	0.46	0.79	1.70	0.472
1937	1.39	4.41	0.51	0.51	0.83	1.76	0.510
1938	1.44	3.45	0.49	0.52	0.81	1.70	0.500
1939	1.41	4.07	0.48	0.52	0.82	1.74	0.494
1940	1.44	3.90	0.52	0.52	0.83	1.72	0.520
1941	1.55	4.45	0.55	0.52	0.90	1.87	0.538

[a] Calculated from index price, *Better Crops with Plant Food*, Feb., 1944.

[b] From *Better Crops with Plant Food*, Feb., 1944.

[c] Calculated from data in table and composition of average ton of fertilizer, Agr. Statistics, 1943. Percentage organic nitrogen from Mehring and Vincent, U. S. D. A. *Circ.* 689.

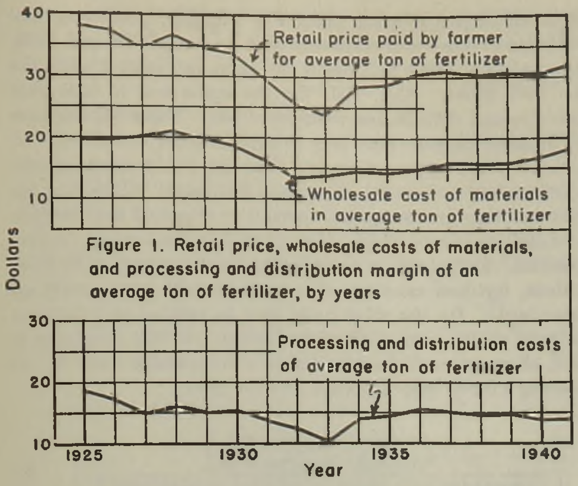

Figure 1. Retail price, wholesale costs of materials, and processing and distribution margin of an average ton of fertilizer, by years

given plant food should represent a weighted average in which consideration has been given to the amount and price of each form of the plant food used. This average price should be determined separately for each year. Actually, only the major forms of nitrogen are included in the prices presented in Table I, and the weightings have not been revised very often. In the case of organics, at least one important material is not included in the data. Potash prices, if properly weighted, would include potassium sulfate and manure salts as well as muriate. The P_2O_5 figures should include double superphosphate and any other sources of P_2O_5. The superphosphate prices are for Baltimore, and obviously the wholesale price at other points, especially interior points, would be materially different.

Nevertheless, the values given in Table I undoubtedly reflect price changes in competitive materials, and further refinement is not likely to change the data or the interpretations from them materially.

All fertilizer ingredients, organic nitrogen materials excepted, have declined in price during the last twenty years. Taking the 1925 prices as a basis, chemical nitrogen was 48% lower in 1940 than in 1925; phosphoric acid from superphosphate was 13% lower, and potash from muriate was 10% lower. With these decreases in all components, the composite retail price per unit of plant food (*1*) fell 33% from 1925 to 1940—a sizable decline as compared to changes in wholesale prices of fertilizer materials.

Table II. Retail Price, Wholesale Cost of Materials, and Processing and Distribution Costs of an Average Ton of Fertilizer[a]

Year	Retail Price Paid by Farmers ($)	Wholesale Cost of Materials[b]	Processing and Distribution Costs
1925	$38.30	$19.60	$18.70
1926	36.60	19.53	17.07
1927	34.80	19.82	14.98
1928	36.90	20.81	16.09
1929	34.70	19.76	14.94
1930	33.80	18.59	15.21
1931	29.90	16.35	13.55
1932	25.70	13.35	12.35
1933	23.80	13.70	10.10
1934	28.20	14.43	13.77
1935	28.50	14.13	14.37
1936	30.10	14.89	15.21
1937	30.80	15.87	14.93
1938	30.20	15.69	14.51
1939	30.50	15.88	14.62
1940	30.30	16.58	13.72
1941	31.70	17.99	13.71

[a] Transportation, processing, and distribution costs include freight on materials (superphosphate, potash, and nitrogen) from ports to interior plants, or, in the case of superphosphate, higher production costs at interior plants due to the freight on rock and sulfur; therefore, these figures are a little higher than those which may be calculated from retail price schedules.
[b] From data in Table I, footnote [c].

The wholesale cost of materials in the average ton of fertilizer, the retail price per ton, and the difference between these two (processing and distribution costs) are given in Table II for 1925 to 1941. The trends are shown graphically in Figure 1. Retail prices per ton from 1936 to 1939 averaged about 14% lower than in the years 1927 to 1930. Wholesale prices per ton were 25% lower. In both periods compared, the processing and distribution margin remained essentially constant at 15 dollars per ton.

INFLUENCE OF WHOLESALE PRICES ON NITROGEN CONTENT

As previously indicated, the wholesale price of fertilizer materials has shifted materially during the last twenty years. The greatest lasting change has been in the cost of chemical nitrogen. Fertilizer consumption statistics for 1925 to 1941 are given in Table III. It is apparent that the proportion of nitrogen in fertilizers has also changed. Tables I and III may be used to compare the changes in nitrogen prices with the quantities of nitrogen used in fertilizers.

Table III. Average Plant-Food Content and Tonnage of Commercial Fertilizers Consumed in the United States[a]

Year	% N	% P_2O_5	% K_2O	Tonnage
1925	3.74	9.12	3.79	7,456,000
1926	3.80	9.32	3.85	7,525,000
1927	3.98	9.43	3.79	7,073,000
1928	4.17	9.46	4.06	8,201,000
1929	4.29	9.43	4.12	8,283,000
1930	4.47	9.41	4.20	8,407,000
1931	4.60	9.34	4.20	6,574,000
1932	4.66	9.01	4.18	4,698,000
1933	4.70	9.07	4.35	5,294,000
1934	4.74	9.12	4.52	5,809,000
1935	4.79	9.18	4.72	6,390,000
1936	4.87	9.19	4.82	7,201,000
1937	4.91	9.25	4.96	8,380,000
1938	5.00	9.23	5.14	7,676,000
1939	5.04	9.17	5.23	7,739,000
1940	5.18	9.30	5.39	8,100,000
1941	5.38	9.25	5.47	8,432,000

[a] Includes Hawaii and Puerto Rico; excludes phosphates distributed by government agencies. Data taken from Agr. Statistics, 1942 and 1943.

Table IV. Nitrogen and Other Plant Food in Relation to Plant-Food Prices[a]

Year	$\frac{N_p}{(P_2O_5 + K_2O)_p}$	$\frac{100\ N}{(P_2O_5 + K_2O)}$	$\frac{100\ N^*}{(P_2O_5 + K_2O)}$	Difference
1926	5.22	28.8	30.1	−1.3
1927	5.22	30.1	30.1	0
1928	5.17	30.9	30.2	+0.7
1929	4.57	31.6	31.6	0
1930	4.13	32.8	32.7	+0.1
1931	3.82	33.8	33.7	+0.1
1932	3.06	35.3	36.4	−1.1
1933	2.73	34.9	38.0	−3.1
1934	3.19	34.8	35.9	−1.1
1935	3.44	34.4	34.9	−0.5
1936	3.52	34.8	34.7	+0.1
1937	3.52	34.6	34.6	0
1938	3.42	34.8	35.0	−0.2
1939	3.46	34.9	34.9	0
1940	3.41	35.3	35.0	+0.3
1941	3.39	36.4	35.1	+1.3

[a] Two-year average prices used.
* Calculated from Equation 2.

A considerable portion of the fertilizer materials sold to farmers in mixed fertilizers in a given year is bought by manufacturers under 12-month contracts at prices prevailing when the contract is made. Thus, it would be expected that prices of both the previous year and the current year would be effective in determining the composition of the fertilizer. The ratio of nitrogen price (two-year average) to other plant-food price (two-year average) is given in Table IV, along with the ratio of nitrogen consumption to other plant-food consumption for the years 1925 to 1941. These ratios are compared graphically in Figure 2. From the nature of the ratios it would be expected that their relation could be expressed by an equation of the type,

$$y = ax^n$$

since, as the ratio plotted as abscissa approaches zero, the ratio plotted as ordinate should approach infinity as a limit and vice versa. These conditions have been imposed upon the curve drawn.

The theoretical relation is:

$$\frac{100\ \mathrm{N}}{\mathrm{P_2O_5 + K_2O}} = 54.1\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} \qquad (2)$$

where p = price

The calculated value of 100 N/(P_2O_5 + K_2O) is given in Table IV for comparison with the reported value. The data fit the theoretical relation reasonably well.

From Equation 2,

$$\frac{\mathrm{N}}{\mathrm{P_2O_5 + K_2O}} = 0.541\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355}$$

$$\frac{\mathrm{N}}{\mathrm{P_2O_5 + K_2O}} + 1 = 0.541\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} + 1$$

$$\frac{\mathrm{N}}{\mathrm{P_2O_5 + K_2O}} + \frac{\mathrm{P_2O_5 + K_2O}}{\mathrm{P_2O_5 + K_2O}} = 0.541\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} + 1$$

$$\frac{\mathrm{N + P_2O_5 + K_2O}}{\mathrm{P_2O_5 + K_2O}} = 0.541\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} + 1$$

$$\frac{\mathrm{P_2O_5 + K_2O}}{\mathrm{N + P_2O_5 + K_2O}} = \frac{1}{0.541\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} + 1}$$

$$1 - \frac{\mathrm{N}}{\mathrm{N + P_2O_5 + K_2O}} = \frac{1}{0.541\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} + 1}$$

it follows, then, that

$$\frac{100\ \mathrm{N}}{\mathrm{N + P_2O_5 + K_2O}} = 100 - \frac{10{,}000}{54.1\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\right]^{-0.355} + 100} \qquad (3)$$

Equation 3 expresses nitrogen as a percentage of the total plant food in terms of nitrogen and other plant-food prices. This relation is shown graphically in Figure 3. The reported data are plotted also for comparison. The relation is almost perfect for ten of the sixteen years and is reasonably good for all years. Comparison of Figure 3 with Figure 1 shows that the years in which the processing and distribution costs were reasonably constant (1927, 29, 30, 36, 37, 38, 39) fit Equation 3 remarkably well. This suggests that the relation could be improved by introducing processing and distribution costs into the equation. It is obvious, however, that other factors affect the relation also. For example, processing and distribution costs were relatively high in both 1926 and 1928, yet one of these years falls below the curve in Figure 3 while the other falls above. Also, 1931 fits the curve and in that year processing and distribution costs were low. Table III suggests that fertilizer tonnage may help to explain these variations. A priori, it would appear that low tonnage would work against factors tending to increase nitrogen in fertilizers. (Low tonnage means low farm incomes, and it would be expected that farmers would shift to lower-nitrogen mixed fertilizers and even to superphosphate, chiefly because these sell at lower ton prices; by buying them, fertilizer rates per acre could be kept more nearly up to standard.) On the other hand, low processing and distribution costs would work with these factors. If this reasoning is sound, all years could be adjusted to a comparable basis by introducing a factor into Equation 3 of the type:

$$\left[\frac{\left(\frac{\text{tonnage in base year}}{\text{tonnage in given year}}\right)}{\left(\frac{\text{processing and distribution costs in base year}}{\text{processing and distribution costs in given year}}\right)}\right]^n \qquad (4)$$

As was true with prices, it would be expected that a better factor would be obtained if averages of previous and present year's values were used. The factor for Equation 4, henceforth identified as $(\text{ton/P.D.})^n$, was evaluated for the data at hand according to the relation:

$$(\text{Ton/P.D.})^n = \left[\frac{\left(\frac{\text{av. 1936–37 tonnage}}{\text{2-yr. av. tonnage}}\right)}{\left(\frac{\text{av. 1936–37 processing and distributing costs}}{\text{2-yr. av. processing and distribution costs}}\right)}\right]^n \qquad (5)$$

and numerical values for (Ton /P.D.) are given in Table V.

Returning to Equation 2, we may place

$$\frac{100\ \mathrm{N}}{\mathrm{P_2O_5 + K_2O}} = a\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\ (\text{Ton/P. D.})^n\right]^m \qquad (6)$$

The best values of a, n, and m in Equation 6 may be determined as closely as desired by graphical analysis using logarithmic coordinates and trial values of n. The relation,

$$\frac{100\ \mathrm{N}}{\mathrm{P_2O_5 + K_2O}} = 50.7\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\ (\text{Ton/P.D.})^{0.6}\right]^{-0.304} \qquad (7)$$

was accepted. Equation 8 may then be developed from 7 in the same way Equation 3 was developed from 2:

$$\frac{100\ \mathrm{N}}{\text{T.P.F.}} = 100 - \frac{10{,}000}{50.7\left[\frac{\mathrm{N}_p}{(\mathrm{P_2O_5 + K_2O})_p}\ (\text{Ton/P.D.})^{0.6}\right]^{-0.304} + 100} \qquad (8)$$

This relation is shown graphically in Figure 4. The reported data, as a whole, fit this relation somewhat better than they did Equation 3. Considerable improvement was made for 1926, 28, 32, 33, 34, and 41; the fit was slightly poorer for 1929, 30, and 36. The values of percentage nitrogen in the total plant food calculated from Equations 3 and 8 are compared with the reported value in Table V.

Effect of Assumed Price Changes on Proportion of Nitrogen in Fertilizers. In 1937 the nitrogen content of the total plant food was 25.7%. The average 1936–37 nitrogen price per unit was $1.73 and the average 1936–37 (P_2O_5 + K_2O) price was $0.491 per unit. A reduction of 20% in the nitrogen price, other conditions remaining the same, in 1937 would have

Table V. Nitrogen Content of Total Plant Food

Year	Ton/P.D.	% N in T.P.F.		
		Eq. 3	Reptd.	Eq. 8
1926	1.226	23.1	22.4	22.9
1927	1.127	23.1	23.1	23.1
1928	1.052	23.2	23.6	23.4
1929	0.967	24.0	24.0	24.3
1930	0.930	24.7	24.7	25.0
1931	0.996	25.2	25.3	25.3
1932	1.214	26.7	26.1	25.9
1933	1.141	27.5	25.9	26.7
1934	1.078	26.4	25.8	26.0
1935	1.183	25.9	25.6	25.2
1936	1.120	25.7	25.8	25.3
1937	1.000	25.7	25.7	25.7
1938	0.943	25.9	25.8	26.1
1939	0.973	25.9	25.9	25.9
1940	0.918	25.9	26.1	26.2
1941	0.852	26.0	26.7	26.5

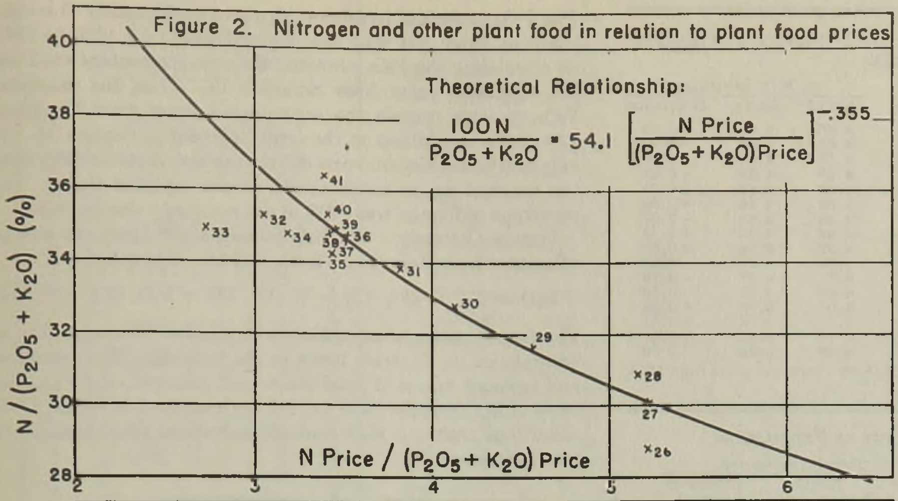
Figure 2. Nitrogen and other plant food in relation to plant food prices

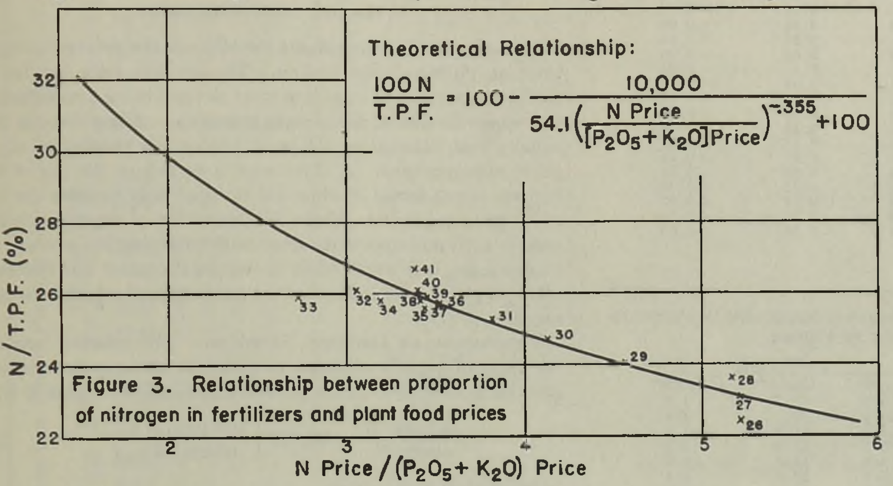
Figure 3. Relationship between proportion of nitrogen in fertilizers and plant food prices

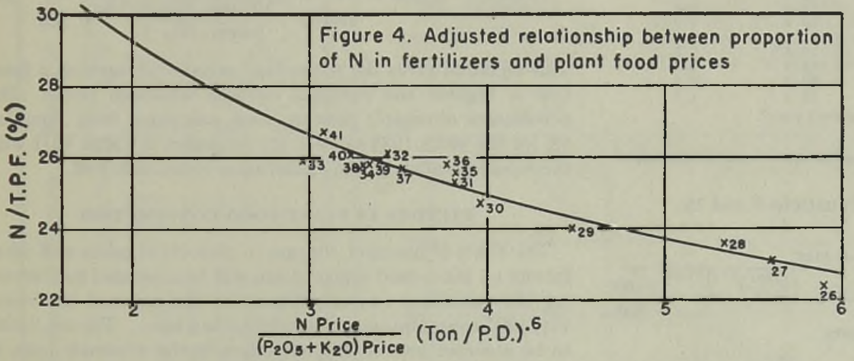
Figure 4. Adjusted relationship between proportion of N in fertilizers and plant food prices

resulted in a nitrogen content in the total plant food of 27.1%, according to Equation 8. Before we can evaluate the effect of this increased proportion of nitrogen on nitrogen consumption, it is necessary to know the influence of price changes on the total plant-food content of fertilizers.

PLANT-FOOD CONTENT OF FERTILIZERS

Total Content. The change in total plant-food content of fertilizers with time is shown in Figure 5. While there has been an increase with time, it is evident that there have been disturbing influences. Using the same reasoning as above, it would appear that fertilizer tonnage and processing and distribution costs would influence the relation between plant-food content of fertilizers and time. If this is true and the relation is linear, as it appears to be, the two years 1931 and 1937 can be used to determine the linear relation since the (Ton/P.D.) factor is one in both of these years. The relation so determined is

$$\text{T.P.F.} = 0.163t + 17.33 \quad (9)$$

where t = time in years from 1926

This relation is also shown in Figure 5. Introducing the factor $(\text{Ton/P.D.})^n$ into Equation 9,

$$\text{T.P.F.} = (0.163t + 17.33) \; (\text{Ton/P.D.})^n \quad (10)$$

From Equation 10 it follows that

$$\log \frac{\text{T.P.F.}}{0.163t + 17.33} = n \log (\text{Ton/P.D.}) \quad (11)$$

Since this equation is linear in logarithmic coordinates, n may be evaluated empirically. Relation 10 is found to be

$$\text{T.P.F.} = (0.163t + 17.33)/ (\text{Ton/P.D.})^{0.125} \quad (12)$$

This relation is also shown in Figure 5, and the calculated and reported values of total plant-food content of fertilizers are compared in Table VI for 1926 to 1941. Relation 12 fits the reported data so perfectly in all years except 1935 and 1936 as to suggest possible error in the reported data (probably processing and distributing costs) for 1935. (Since two-year averages were used, an error in 1935 would affect both 1935 and 1936.) Even in 1935 and 1936 the calculated and reported values differ by only 1.5% of the reported value.

The fact that the total plant-food content of fertilizers can be expressed as a time relation [fertilizer prices exert only a secondary influence in the (Ton/P.D.) factor] suggests that research and education, both agronomic and technological, have played large parts in increasing the total plant food in fertilizers.

Table VI. Total Plant Food and Nitrogen Contents of Fertilizers

Year	T.P.F.			% N in Fertilizers		
	Calcd.[a]	Reptd.	Difference	Calcd.[b]	Reptd.	Difference
1926	16.91	16.97	−0.06	3.85	3.80	+0.05
1927	17.21	17.20	+0.01	3.95	3.98	−0.03
1928	17.55	17.69	−0.14	4.11	4.17	−0.06
1929	17.89	17.84	+0.05	4.36	4.29	+0.07
1930	18.13	18.08	+0.05	4.53	4.47	+0.06
1931	18.15	18.14	+0.01	4.56	4.60	−0.04
1932	17.87	17.85	+0.02	4.59	4.66	−0.07
1933	18.17	18.12	+0.05	4.86	4.70	+0.16
1934	18.47	18.38	+0.09	4.81	4.74	+0.07
1935	18.40	18.69	−0.29	4.63	4.79	−0.16
1936	18.67	18.88	−0.21	4.71	4.87	−0.16
1937	19.12	19.12	0.00	4.91	4.91	0.00
1938	19.41	19.37	+0.04	5.06	5.00	+0.06
1939	19.51	19.44	+0.07	5.05	5.04	+0.01
1940	19.84	19.87	−0.03	5.19	5.18	+0.01
1941	20.19	20.10	+0.09	5.38	5.38	0.00

[a] T.P.F = $(0.163t + 17.33)/(\text{Ton/P.D.})^{0.125}$, where t = years from 1926.

[b] By Equation 13.

Table VII. P_2O_5 Content of Fertilizers

Year	$\frac{N_p}{(P_2O_5)_p}$*	% P_2O_5 in Fertilizers		
		Calcd.[a]	Reptd.	Difference
1926	5.20	9.18	9.32	−0.14
1927	5.37	9.34	9.43	−0.09
1928	5.43	9.58	9.46	+0.12
1929	4.74	9.35	9.43	−0.08
1930	4.35	9.17	9.41	−0.24
1931	4.19	9.24	9.34	−0.10
1932	3.48	9.00	9.01	−0.01
1933	3.16	8.94	9.07	−0.13
1934	3.44	9.10	9.12	−0.02
1935	3.35	8.85	9.18	−0.33
1936	3.40	8.95	9.19	−0.24
1937	3.49	9.14	9.25	−0.11
1938	3.46	9.20	9.23	−0.03
1939	3.57	9.44	9.17	+0.27
1940	3.46	9.39	9.30	+0.09
1941	3.34	9.34	9.25	+0.09

* Two-year average prices.

[a] By Equation 15.

Table VIII. Percentage of Organic Nitrogen in Fertilizers in Relation to Prices

Year	$\frac{(O.N.)_p}{(C.N.)_p}$*	$\frac{O.N.}{C.N.}$	O.N./T.N.		
			Reptd.	Calcd.[a]	Difference
1925	160	31.9	24.2	25.7	1.5
1926	170	29.0	22.5	23.7	1.2
1927	185	29.5	22.8	21.3	−1.5
1928	229	20.1	16.7	16.3	−0.4
1929	240	18.5	15.6	15.3	−0.3
1930	227	18.2	15.4	16.5	1.1
1931	197	24.8	19.9	19.7	−0.2
1932	149	34.3	25.6	28.3	2.7
1933	162	26.4	20.9	25.2	4.3
1934	216	23.0	18.7	17.6	−1.1
1935	250	20.0	16.7	14.5	−2.2
1936	273	20.2	16.8	12.9	−3.9
1937	299	14.0	12.3	11.4	−0.9
1938	277	14.7	12.8	12.5	−0.3
1939	265	14.0	12.3	13.4	1.1
1940	281	13.1	11.6	12.3	0.7
1941	281	11.9	10.6	12.3	1.7

* Two-year average prices (previous and present year).

[a] By Equation 18.

Nitrogen Content. Combining Equations 8 and 12,

$$N = \frac{0.163t + 17.33}{\left(\frac{\text{Ton}}{\text{P.D.}}\right)^{0.125}} - \frac{16.3t + 1733}{\left(\frac{\text{Ton}}{\text{P.D.}}\right)^{0.125} 50.7 \left[\frac{N_p}{(P_2O_5 + K_2O)_p} \left(\frac{\text{Ton}}{\text{P.D.}}\right)^{0.6}\right]^{-0.304} + 100} \tag{13}$$

where N = nitrogen content of fertilizers

The calculated and reported nitrogen contents are compared in Table VI for the years 1926 to 1941. The agreement is exceptionally good.

Phosphoric Acid Content. The relation between the ratio of nitrogen to P_2O_5 in fertilizers and the ratio of their prices is shown graphically in Figure 6. The average relation is:

$$\frac{100\ N}{P_2O_5} = 97.38 \left[\frac{N_p}{(P_2O_5)_p} (\text{Ton/P.D.})^{0.6}\right]^{-0.475} \tag{14}$$

from which it follows that P_2O_5 content of fertilizers is given by

$$P_2O_5 = 1.027\ N \left[\frac{N_p}{(P_2O_5)_p} (\text{Ton/P.D.})^{0.6}\right]^{0.475} \tag{15}$$

The P_2O_5 content of fertilizers calculated by Equation 15 is compared in Table VII with the reported values for 1926 to 1941. In calculating the P_2O_5 contents, the nitrogen content used was the calculated value from Equation 13. Thus, the calculated P_2O_5 contents contain the accumulated errors from Equations 12 and 13, in addition to the errors inherent in relation 15. In only four of the sixteen years did the calculated values differ from the reported by as much as 2% of the reported value. The maximum difference was 3.6% of the reported value in 1935.

Potash Content. The K_2O content of fertilizers can now be calculated from Equations 12, 13, and 15. The relation is

$$K_2O = \text{T.P.F. (Eq. 12)} - \text{N (Eq. 13)} - P_2O_5\ \text{(Eq. 15)} \tag{16}$$

The potash contents calculated from relation 16 can be only as accurate as the separate items in the relation. The calculated and reported values of total plant-food, nitrogen, and P_2O_5 contents of fertilizers for 1926 to 1941 are compared in Figure 7. It is obvious that the K_2O contents calculated from relation 16 are satisfactory.

AVERAGE NITROGEN PRICE

It is now possible to evaluate the effect of the average nitrogen price on nitrogen consumption. The average price can be reduced in a number of ways, the most obvious being a reduction in the wholesale cost of all nitrogen materials. A less obvious, but equally real, method would be to reduce the proportion of organic nitrogen used. A third way is to reduce the use of the highest priced forms of chemical nitrogen and increase the use of lower priced forms. Since the proportion of organic nitrogen used is such an important factor in determining the average nitrogen price, it is worth while to inquire if organic and chemical nitrogen prices have influenced the proportion of organic nitrogen used.

Proportion of Organic Nitrogen. The relation between the ratio of organic nitrogen to chemical nitrogen in fertilizers and the ratio of their prices (shown graphically in Figure 8) is:

$$\frac{100\ \text{org. N}}{\text{chem. N}} = 88{,}100 \left[\frac{100\ (\text{org. N})_p}{(\text{chem. N})_p}\right]^{-1.55} \tag{17}$$

from which it follows that

$$\frac{100\ \text{org. N}}{\text{total N}} = 100 - \frac{10{,}000}{88{,}100 \left[\frac{100\ (\text{org. N})_p}{(\text{chem. N})_p}\right]^{-1.55} + 100} \tag{18}$$

This equation gives the percentage organic nitrogen as a function of organic and chemical nitrogen wholesale prices. The percentages of organic nitrogen used, calculated from Equation 18, for the years 1925 to 1941 are compared in Table VIII with the reported values. The values agree reasonably well.

FACTORS IN PLANT-FOOD CONSUMPTION

The effect of assumed changes in plant-food prices and other factors on plant-food consumption will be evaluated by comparing the calculated consumption under the assumed conditions with 1937 consumption and conditions as a base. The conditions to be assumed are: a 20% reduction in the wholesale price of chemical nitrogen, a 20% reduction in the wholesale price of all nitrogen, a 20% reduction in the wholesale prices of P_2O_5 and K_2O, a 20% reduction in the wholesale prices of chemical nitrogen, P_2O_5, and K_2O, and a 20% reduction in the wholesale price of chemical nitrogen accompanied by a 20% increase in the total plant-food content of fertilizers. In order that valid comparisons can be made, it is necessary to adjust 1937 conditions to fit equations developed above, since effects of assumed conditions are to be evaluated on the basis of these equations.

The reported and adjusted 1937 conditions and consumption and the assumed case of a 20% reduction in chemical nitrogen prices will be given in some detail to illustrate the method of

Table IX. Influence of Wholesale Prices of Plant Food and Other Factors on the Consumption of Plant Food in the United States

Case No.	Assumed Conditions	Wholesale Price per Unit					Org. N, %	Fertilizer Compn., %				Indicated Consumption for 1937[a], Tons					
		Chem. N	Org. N	All N	P_2O_5	K_2O		T.P.F.	N	P_2O_5	K_2O	Fertilizers	Org. N	Chem. N	Total N	P_2O_5	K_2O
1	1937, actual	$1.39	$4.41	$1.76	$0.51	$0.51	12.3	19.12	4.91	9.25	4.96	8,380,000	50,600	361,000	411,600	775,100	415,600
2	1937, adjusted to fit equations	1.39	4.41	1.70	0.51	0.51	10.4	19.12	4.99	9.07	5.06	8,429,000	43,800	376,800	420,600	764,500	426,500
3	20% reduction in 1937 wholesale price of chem. N	1.11	4.41	1.36	0.51	0.51	7.4	19.12	5.22	8.55	5.35	8,875,000 (+5.3%)	34,600	428,700	463,300 (+10.2%)	758,800 (−0.7%)	474,800 (+11.3%)
4	20% reduction in 1937 wholesale price of all N	1.11	3.53	1.36	0.51	0.51	10.4	19.12	5.22	8.55	5.35	8,875,000 (+5.3%)	48,200	415,100	463,300 (+10.2%)	758,800 (−0.7%)	474,800 (+11.3%)
5	20% reduction in 1937 wholesale prices of P_2O_5 and K_2O	1.39	4.41	1.70	0.41	0.41	10.4	19.12	4.72	9.50	4.90	8,924,000 (+5.9%)	43,700	377,500	421,200 (+0.14%)	847,800 (+10.9%)	437,300 (+2.5%)
6	20% reduction in 1937 wholesale prices of chem. N, P_2O_5, and K_2O	1.11	4.41	1.36	0.41	0.41	7.4	19.12	4.99	9.07	5.06	9,391,000 (+11.4%)	34,700	433,900	468,600 (+11.4%)	851,800 (+11.4%)	475,200 (+11.4%)
7	20% reduction in 1937 wholesale price of chem. N, 20% increase in T.P.F. in fertilizers	1.11	4.41	1.36	0.51	0.51	7.4	22.94	6.26	10.26	6.42	8,089,000 (−4.0%)	37,200	469,200	506,400 (+20.4%)	829,900 (+8.6%)	519,300 (+21.8%)

[a] Based on 1937 actual expenditures for fertilizers. Percentages given in parentheses indicate changes from the adjusted 1937 conditions; plus indicates an increase, minus indicates a decrease.

calculation. Table IX summarizes these and other assumed cases. (See page 288 for cases I, II, and III.)

Cases 4, 5, and 6 in Table IX were included for comparison with the more probable cases, 3 and 7 A 20% reduction in the wholesale price of all nitrogen, case 4, does not increase plant-food consumption above the increase obtained with a 20% decrease in the wholesale price of chemical nitrogen only, case 3. A 20% reduction in the wholesale prices of P_2O_5 and K_2O would have almost no influence on the consumption of nitrogen and potash, but phosphoric acid consumption would be increased about 11%. Comparison of cases 3, 6, and 7 shows that an increase of 20% in the total plant-food content of fertilizers would increase the plant-food consumption almost as much as that of a 20% reduction in the wholesale prices of all plant food.

The probabilities are good that the assumed conditions in case 7, a 20% reduction in the wholesale price of chemical nitrogen and a 20% increase in the plant-food content of fertilizers, can be achieved in the postwar period. The assumed reduction of 20% in the wholesale price of chemical nitrogen, while arbitrary, seems reasonable in view of recent reductions in the price of anhydrous ammonia and ammonia solutions. It should be remembered that the assumed price of chemical nitrogen is the average price, and that this average can be lowered by using greater quantities of lower priced materials. Increasing the total plant-food content of fertilizers to 23% is technically feasible and may be achieved by progressive fertilizer grade programs in the several states. The increased consumption of plant food that would have occurred in 1937 under the assumptions of case 7 is equivalent to 1,100,000 tons of an 8-6-8 fertilizer.

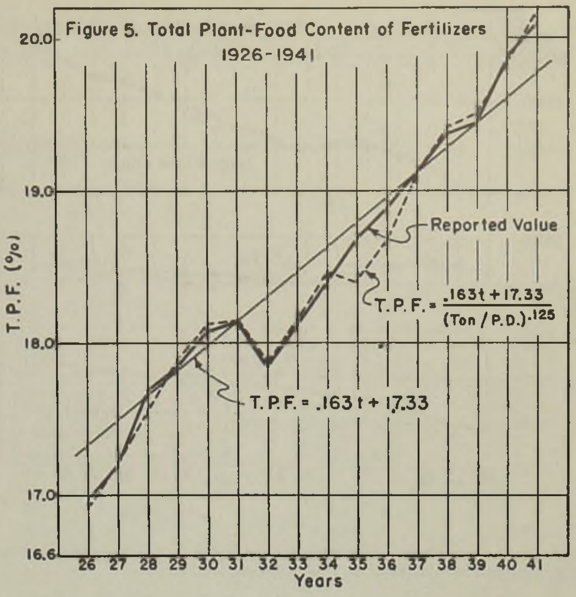
Figure 5. Total Plant-Food Content of Fertilizers 1926-1941

CONCLUSIONS

The relations developed in this paper have been used to estimate the effect of decreased wholesale prices of plant food on plant-food consumption. Using 1937 conditions as a basis of comparison, it is indicated that a 20% reduction in the whole-

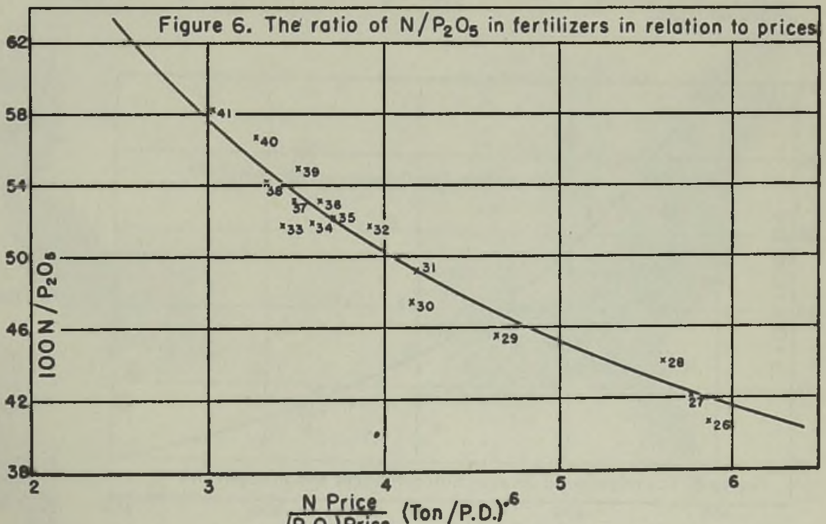
Figure 6. The ratio of N/P_2O_5 in fertilizers in relation to prices

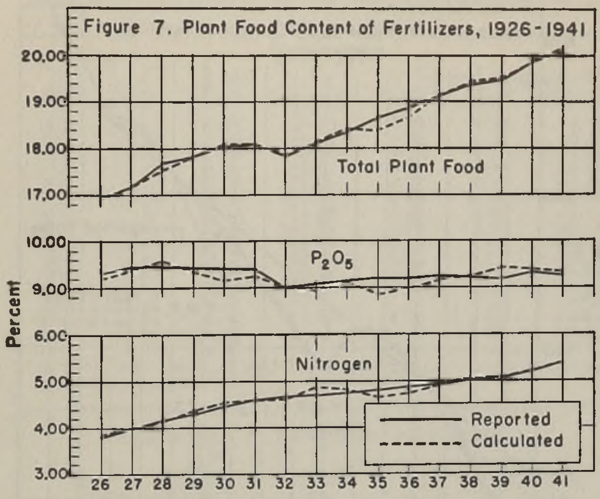
Figure 7. Plant Food Content of Fertilizers, 1926-1941

sale price of chemical nitrogen would have resulted in the following changes in plant-food consumption in 1937:

		Tons	%
Chemical N	Increase	51,900	13.8
Organic N	Decrease	9,200	21.0
P_2O_5	Decrease	5,700	0.7
K_2O	Increase	48,300	11.3

A 20% reduction in the wholesale price of chemical nitrogen coupled with an increase of 20% in the plant-food content of fertilizers, would have resulted in the following changes in consumption in 1937:

		Tons	%
Chemical N	Increase	92,400	24.5
Organic N	Decrease	6,600	15.1
P_2O_5	Increase	65,400	8.6
K_2O	Increase	92,800	21.8

These increased quantities of plant food, equivalent to 1,100,000 tons of an 8-6-8 fertilizer, would have been purchased by farmers for the same expenditure for fertilizers as was made in 1937.

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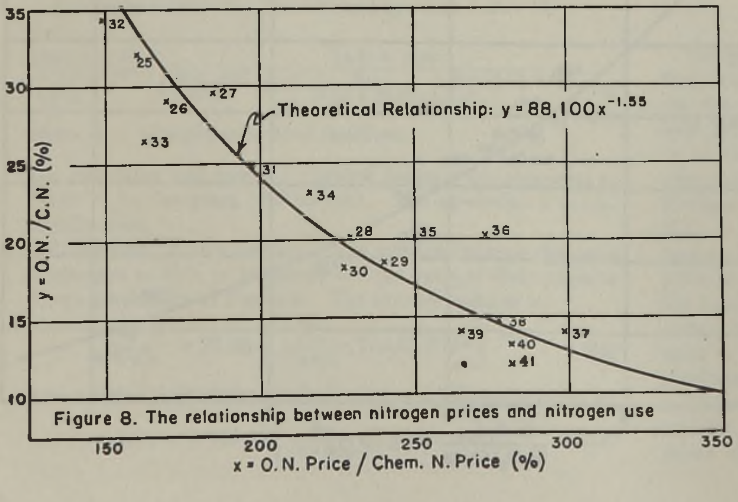
Figure 8. The relationship between nitrogen prices and nitrogen use

CASE I. 1937 Prices and Consumption.

A. Plant-food cost per ton:

9.25 units P_2O_5 at	$0.51	=	$ 4.72
4.96 units K_2O at	0.51	=	2.53
4.31 units chem. N at	1.39	=	5.99
0.60 unit org. N at	4.41	=	2.65
19.12 units plant food			$15.89

B. Retail price of average ton of fertilizer: $30.83 (from Mehring and Shaw, *1*)

C. Tonnage:

Fertilizers	8,380,000
Chemical N	361,000
Organic N	50,600
Total N	411,600
P_2O_5	775,100
K_2O	415,600

CASE II. Adjusted 1937 Conditions.

A. Changes from 1937 conditions:

	1937 Conditions	Adjusted Conditions (1-Yr. Prices)
Organic N, %	12.3	10.4 (Eq. 18)
Av. N price	$1.76	$1.70
N content of fertilizer, %	4.91	4.99 (Eq. 13)
T.P.F. content of fertilizer, %	19.12	19.12 (Eq. 12)
P_2O_5 content of fertilizer, %	9.25	9.07 (Eq. 15)
K_2O content of fertilizer, %	4.96	5.06 (Eq. 16)

B. Plant-food cost per ton:

9.07 units P_2O_5 at	$0.51	=	$ 4.63
5.06 units K_2O at	0.51	=	2.58
4.47 units chem. N at	1.39	=	6.21
0.52 unit org. N at	4.41	=	2.29
19.12 units plant food			$15.71

C. Retail price of average ton of fertilizer:

$30.65 = $30.83 − ($15.89 − $15.71)

D. Tonnage (based on $258,355,000 spent for fertilizers):

Fertilizers	8,429,000
Chemical N	376,800
Organic N	43,800
Total N	420,600
P_2O_5	764,500
K_2O	426,500

CASE III. 20% Reduction in Wholesale Prices of Chemical Nitrogen.

A. Calculations:

Organic N, %	7.4 (Eq. 18)
Av. N price per unit	$1.36
T.P.F. content of fertilizer, %	19.12 (Eq. 12)
N content of fertilizer, %	5.22 (Eq. 13)
P_2O_5 content of fertilizer, %	8.55 (Eq. 15)
K_2O content of fertilizer, %	5.35 (Eq. 16)

B. Plant-food cost per ton:

8.55 units P_2O_5 at	$0.51	=	$ 4.36
5.35 units K_2O at	0.51	=	2.73
4.83 units chem. N at	1.11	=	5.36
0.39 unit org. N at	4.41	=	1.72
19.12 units plant food			$14.17

C. Retail price of average ton of fertilizer:

$29.11 = $30.83 − ($15.89 − $14.17)

D. Tonnage (based on $258,355,000 spent for fertilizer):

	Tons	% Increase or Decrease
Fertilizers	8,875,000	+ 5.3
Chemical N	428,700	+13.8
Organic N	34,600	−21.0
Total N	463,300	+10.2
P_2O_5	758,800	− 0.7
K_2O	474,800	+11 3

Fertilizer Nitrogen Consumption

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THE consumption of commercial nitrogen per acre of cultivated land varies tremendously from state to state. Nitrogen consumption also varies, but much less markedly, in the same state from year to year. In a general way something is known of the reasons for these differences in rate of consumption of nitrogen, but much misinformation on the subject is current. For example, from time to time the statement appears that the Central states use so little fertilizer because they have been farmed only a relatively short time, and that the Atlantic Coastal states use so much because their soils have been exhausted by hundreds of years of continuous cropping. Whatever may be the case for other plant nutrients, these statements are not true with regard to nitrogen.

The purpose of this paper is to give the results of an attempt to evaluate quantitatively the importance of several factors responsible for differences in rate of nitrogen consumption in different places and different years.

The consumption of commercial fertilizer nitrogen in the United States increased from 19,000 tons in 1880 to about 400,000 tons annually in recent years. Consumption is expected to be about 600,000 tons in 1944 and will probably exceed this tonnage in 1945. Factors affecting fertilizer nitrogen consumption may be divided for convenience into two groups: (1) those that affect total consumption of nitrogen and (2) those that affect the kind of nitrogen consumed. A study was made of the following factors: group 1—cash farm income in the previous season, proportion of previous year's income remaining after expense of production has been deducted, prospects for farm income in the same season, cost of a unit of nitrogen relative to that of a unit each of P_2O_5 and K_2O, quantity of nitrogen naturally present in the soil, climate, and system of farming; group 2—cost per unit of nitrogen in various competing forms, properties relating to use in manufacturing mixed fertilizers, and properties relating to efficiency in promoting crop yields in various soils.

TOTAL CONSUMPTION

The principal factors thought to influence the rate of application of commercial nitrogen may be conveniently classified in two categories. The first includes those factors that are more or less fixed for the area, such as kind of crops usually grown, soil nitrogen content, and quantities of animal manures available for application to cultivated crops. The second category comprises factors that cause the consumption to vary from year to year, such as income of farmer, market prospects, prices, salesmanship, etc.

One of the factors in the first category is the kind of crops. Where truck crops, such as cabbage, celery, sweet corn, etc., are grown extensively for market, relatively high rates of application of nitrogen are commonly used. Generous applications are usually made to other high-value-per-acre crops, such as commercial potatoes, citrus fruits, tobacco, etc. On the other hand, even in regions of nitrogen-deficient soils, the rates of nitrogen application to crops of low acre value, such as field corn and oats, are usually low.

The nitrogen content of the soil is also a factor in determining how much fertilizer nitrogen will be purchased and applied by the farmer. The nitrogen content is usually low in the soils of the Southeast, where commercial nitrogen is almost universally employed in agriculture. These soils were low in nitrogen when the first white settlers arrived, as indicated by the fact that the Indians were utilizing fish in the Atlantic Coastal region to fertilize their crops. When the white man's crops failed, he also learned to use fish for this purpose. On the other hand, the soils of the West Central states are relatively high in nitrogen. The farmers of these states buy comparatively little nitrogen. This relation between soil nitrogen content and fertilizer nitrogen consumption is evident from Figures 1 and 2; however, there are exceptions. For example, the soils of Massachusetts, Connecticut, and Rhode Island contain about as much nitrogen as those of Michigan and Indiana, but use far more commercial fertilizer nitrogen per acre. This higher use may be due to a variety of factors, but a considerable part is believed to result from the high

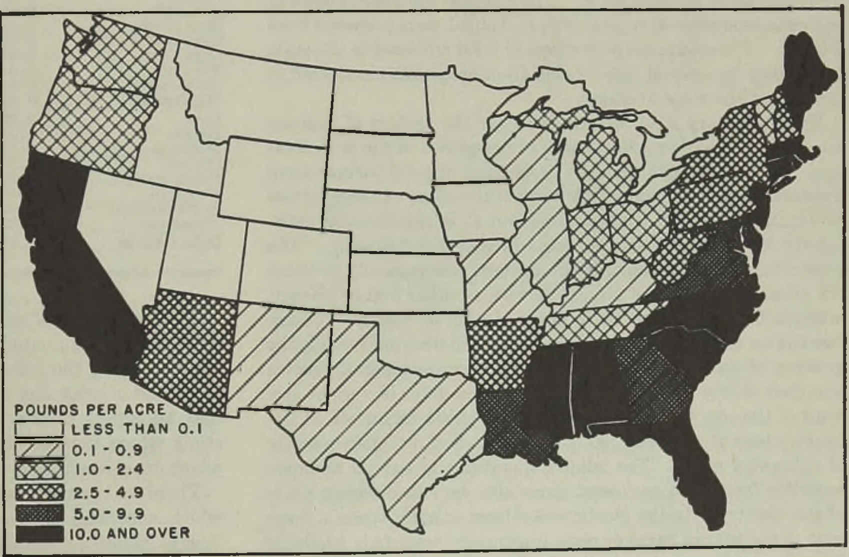

Figure 1. Consumption of Nitrogen in Pounds per Acre of Cropland in 1941

proportion of cultivated land of southern New England devoted to truck crops and cigar wrapper tobacco, both of which yield a high dollar return per acre. Another factor that influences fertilizer nitrogen consumption is the quantity of animal manure available for application to cultivated crops. For example, Parker (*18*) showed that the following quantities of nitrogen were applied to cultivated crops in 1927:

Region	Tons of Nitrogen in: Manure	Tons of Nitrogen in: Fertilizer
New England	28,300	17,256
Middle Atlantic	176,200	39,521
East North Central	278,500	14,643
Southeast	15,534	186,200

From the information now available it is rather difficult to decide the relative importance of the factors just discussed.

PLACE FACTORS

The average nitrogen consumption per acre of harvested cropland in the form of commercial fertilizers is given by states in Table I for the year 1941. These figures were calculated from the total nitrogen consumption published by Mehring and Vincent (*16*) and the sum of the acreages of fifty-two crops in 1941, given by the Bureau of Agricultural Economics (*7*), and those for twenty additional crops in 1940, published in the 1940 Census of Agriculture. The twenty extra crops were added because the published figures for total value, which also are needed in this work, include seventy-two crops and because in a few states some of these additional crops, such as oranges and apples, consume important quantities of nitrogen.

The rate of nitrogen consumption varies from about 40 pounds per acre of harvested cropland annually in Florida to practically none in some of the Mountain states. The principal causes of these great differences in different states are believed to be: differences in value per acre of the crops grown, varying quantities of nitrogen normally present in the soil, and differing systems of farming in the several states. The average crop value per acre was therefore calculated from figures published by the Bureau of Agricultural Economics (*7*) and the results are given in Table I. The average nitrogen content of the soil was estimated in the following manner: The available nitrogen determinations of each soil type were collected from various sources (*1–6*, *8–14*, *17*, *19–24*). The average nitrogen content of the major soil types were then listed for each state. The nitrogen soil map (Figure 2) and estimated state averages given in Table I were prepared from this list. The estimated percentage of total cropland in the state falling into the several major association areas was considered in arriving at the state averages.

No satisfactory data are available for the factors of manure applied per acre of cropland and legumes grown in the crop rotation. It was thought that the proportion of total income from livestock should give some indication of the effect of these factors on fertilizer nitrogen consumption, but it is not entirely satisfactory for several reasons, among which are the following. The livestock system of farming in the Eastern states usually involves the extensive growing of alfalfa, clovers, or other highly efficient nitrogen-fixing legumes on a part of the cropland. Poultry farming on an intensive scale, however, often does not include the growing of any legumes. The kind of legumes generally grown and their ability to fix atmospheric nitrogen differ in various sections of the country. Cattle raising in Florida and much of the country west of meridian 100 is usually carried on independently of cultivated crops. The relative quantities of animal manures available for use on harvested crops also vary in different parts of the country. In the North where farm animals spend a large part of the year in barns or pens, much more manure is available for cultivated crops than in the South where farm animals spend most of the time in pastures or woods.

Comparison of the figures in Table I shows that, in general, high rates of nitrogen consumption correspond to high crop value, low nitrogen content, and low proportion of income from livestock for the same state and vice versa. The simple correlation coefficient between rate of nitrogen consumption and average crop value is +0.728, and between rate of nitrogen consumption and nitrogen content of the soil is −0.372 when values for all states in the table are used. These results may be unreliable, however, for the following reasons. The use of two sets of rates where the units composing the population vary in size may increase or decrease the correlation or even create spurious correlation where none really exists. A number of the West Central and Intermountain states use relatively little fertilizer nitrogen, and what is used is probably on specialized crops or nontypical soils. Such figures might cause errors. The soil data in the table are not so reliable for the Western states as they are for the Eastern.

Table I. Fertilizer Nitrogen Consumption in 1941 per Acre of Harvested Cropland Arranged by States

State	N Consumption, Lb. per Acre	Crop Value per Acre	Av. N Content of Soil, %	Proportion of Total Cash Income from Livestock, %
Florida	39.85	$75.06	0.03	20.2
Rhode Island	24.00	46.23	0.18	68.5
New Jersey	21.66	62.86	0.10	56.4
Connecticut	17.75	66.84	0.18	64.3
South Carolina	16.67	24.15	0.04	18.8
Massachusetts	16.07	56.80	0.18	60.0
North Carolina	15.18	49.31	0.06	14.7
Maine	14.89	40.45	0.18	48.9
California	10.70	79.86	0.06	33.2
Alabama	10.54	25.18	0.05	21.4
Mississippi	10.12	31.97	0.10	16.4
Georgia	8.76	21.16	0.04	22.4
Virginia	8.28	32.20	0.07	48.1
Louisiana	7.63	29.00	0.12	25.0
Maryland	7.31	34.36	0.12	56.4
Delaware	5.85	29.12	0.08	79.5
New Hampshire	3.82	22.09	0.18	77.8
New York	3.78	29.53	0.18	67.9
Pennsylvania	3.08	28.00	0.15	71.4
Arkansas	2.94	34.82	0.11	23.7
Arizona	2.77	60.87	0.05	40.2
West Virginia	2.37	21.99	0.15	71.1
Ohio	2.01	28.79	0.15	69.2
Oregon	1.83	30.95	0.14	51.3
Tennessee	1.43	29.75	0.10	39.1
Vermont	1.37	20.97	0.18	83.5
Michigan	1.19	24.61	0.15	62.7
Indiana	1.13	26.45	0.15	72.1
Washington	1.02	38.25	0.15	40.1
Kentucky	0.90	34.67	0.13	47.0
Texas	0.54	19.68	0.12	41.9
Wisconsin	0.34	20.95	0.15	87.5
Illinois	0.19	28.51	0.21	61.7
Missouri	0.18	19.29	0.17	73.3
New Mexico	0.16	21.23	0.10	67.4
Colorado	0.08	16.15	0.11	57.4
Utah	0.05	27.73	0.10	69.9
Nevada	0.044	15.10	0.10	87.1
Oklahoma	0.043	14.33	0.12	48.4
Minnesota	0.042	15.98	0.27	74.2
Iowa	0.036	24.24	0.25	79.0
Kansas	0.015	12.33	0.17	53.3
Montana	0.014	14.74	0.13	45.9
Idaho	0.003	31.53	0.13	51.9
North Dakota	0.002	12.58	0.29	33.9
Nebraska	0.002	12.15	0.20	69.5
South Dakota	0.001	8.94	0.26	67.0
Wyoming	0.000	15.56	0.12	76.0
United States	2.471	23.54	0.16	54.8

The possibility of spurious correlation due to different size units may be eliminated by using total values for each state and then removing the influence of size by partial correlation. The likelihood of error due to use of figures for nontypical conditions may be largely prevented by selecting only those states for the study where the use of fertilizers is general and typical and in which usage has become stabilized over a long period of years.

There are twenty-five states, all east of the Mississippi River, in which, according to the 1940 Census, 40 % or more of all farmers bought commercial fertilizer for their crops in 1939. A large proportion of the farmers of all these states have used fertilizers extensively for fifty or more years. Fertilizer usage in terms of farm

Table II. Total Fertilizer Nitrogen Consumption, Total Value of Seventy-Two Crops, Total Nitrogen Content of Cultivated Soils in the Top 6-Inch Layer, Total Cash Income from Livestock, and Total Acreage of Seventy-Two Crops, by States in 1941

State	X_1, N Consumption (*16*), Tons	X_2, Crop Value (*7*), 1000 Dollars	X_3, N Content of Soil, 1000 Tons	X_4, Income from Livestock (*7*), 1,000,000 Dollars	X_5, Cropland (*7*), 1000 Acres
Ala.	36,126	172,614	3,427	33	6,854
Conn.	3,406	25,648	691	41	384
Del.	1,111	11,068	304	34	380
Fla.	31,062	116,999	468	30	1,559
Ga.	41,929	185,301	3,503	41	8,758
Ind.	5,741	268,035	15,202	289	10,134
Ky.	2,374	182,603	6,847	95	5,267
La.	15,579	118,351	4,897	33	4,081
Maine	9,120	49,540	2,205	28	1,225
Md.	5,846	55,847	1,950	55	1,625
Mass.	3,789	26,794	849	55	472
Mich.	4,715	195,051	11,886	192	7,924
Miss.	37,077	234,233	7,326	36	7,326
N. H.	744	8,599	701	20	389
N. J.	8,593	49,872	793	69	793
N. Y.	12,914	201,797	12,301	274	6,834
N. C.	47,567	309,001	3,759	44	6,266
Ohio	10,092	289,650	15,089	304	10,059
Pa.	9,352	169,849	9,098	226	6,066
R. I.	628	2,419	94	8	52
S. C.	40,406	117,106	1,940	20	4,849
Tenn.	4,569	190,108	6,398	80	6,389
Vt.	696	21,339	1,832	42	1,017
Va.	15,800	122,925	2,672	77	3,818
W. Va.	1,786	33,184	2,264	37	1,509

income has been stabilized for at least twenty years. The proportion of farmers using fertilizers in the remaining states in 1939 was under 20% in all but Arkansas and California. Accordingly a net correlation study was made from the data in Table II for the twenty-five Eastern states. These states form a solid block of territory, and this area may therefore be handled as a total population study. Figures were used for 1941, because this is the most recent year in which abnormal conditions did not seriously affect either nitrogen usage, crop yields, or crop values.

The correlation coefficients obtained in this study are given in Table III. In this case the simple correlation coefficients do not have very much meaning by themselves, because of the large differences in size between states. The partial or net coefficients, where the effects of other known factors have been removed, have more meaning. High positive correlation exists between factors 2 and 3, 2 and 4, 2 and 5, 3 and 4, 3 and 5, and 4 and 5. When the effects of these intercorrelations are untangled, it appears that both crop value and nitrogen content of soil are about equally correlated with nitrogen consumption. All of the coefficients between factors 1 and 4 (nitrogen consumption and income from livestock) are negative, but when the effects of other factors are removed, the third-order coefficient, $r_{14.235}$, indicates that the effect is small, if any. Thus the data on income from livestock do not serve to show the effect of animal manure and legumes in the rotation on nitrogen consumption. The final answer on these factors will have to await the collection of the proper basic data. There is highly significant positive correlation between income from livestock and nitrogen content of the soil. Which is cause and which effect or the extent to which each affects the other is not clear. The correlation coefficient, $r_{15.234} = +0.431$, shows that small states use proportionately more nitrogen per acre than large states. Otherwise the coefficient would approach +1.000 in value. Although this is a real relation, it is believed to be due only to geographic position or chance, for there is no reason, a priori, why a small state should use proportionately more or less nitrogen than a big one.

The multiple correlation coefficient, $R_{1.2345}$, is 0.909. The size of this coefficient shows that 83% of the variations in the size of nitrogen consumption, X_1 in Table II, are associated with corresponding deviations from the mean values of the other four sets of variates.

The data used in the above analysis are in diverse units—tons, million dollars, thousand acres, etc. To compare more exactly the relative importance of the several factors on nitrogen consumption, it will be necessary to compute beta coefficients. The third-order beta coefficients for the data in Table II follow:

$$\beta_{12.345} = +0.909$$
$$\beta_{13.245} = -1.237$$
$$\beta_{14.235} = -0.063$$
$$\beta_{15.234} = +0.674$$

They show that the soil nitrogen content is most important in determining the consumption of fertilizer nitrogen, because for every standard unit change in soil nitrogen, fertilizer nitrogen consumption changes 1.237 units in the opposite direction. For each standard unit change of the crop value or crop acreage, nitrogen consumption changes 0.909 and 0.674 unit, respectively, in the same direction.

The regression equation expressed in the units of measurement shown in Table II is:

$$X_1 = 0.16067\,X_2 - 3.3088\,X_3 - 31.1797\,X_4 + 2.1268\,X_5 + 3604$$

The use of this equation gives the correct nitrogen consumption in 1941 for the area of twenty-five states used in this study. This equation, however, should not be utilized for estimation purposes without considerable caution. There are probably other factors in the problem, such as quantities of manure available for cultivated crops, kinds and quantities of legumes grown in the rotation, and possibly others that have not been evaluated. The equation will give the best estimate of nitrogen consumption only for states with large areas and fairly homogeneous soil and crop conditions. It will give results that are too high for relatively small acreages, because of the constant term of 3604 tons of nitrogen. The equation in effect says that, even if the conditions covered by the factors employed were such that no nitrogen would be bought, 3604 tons will be consumed nevertheless. This may be true on the average for large states but obviously could not be true for a relatively small area, such as a county of 1000 acres. If this equation should be used for any other year than 1941, the substituted data must be for the year in question in order that the results have any meaning.

Table III. Correlation Coefficients Showing Association[a] between X_1 (Total Nitrogen Consumption by States, 1941) and X_2, X_3, X_4, and X_5

Variate	Zero Order[b]		First Order		Second Order		Third Order	
	Subscript	Coefficient	Subscript	Coefficient	Subscript	Coefficient	Subscript	Coefficient
X_2	12	+0.539	12.3	+0.881	12.35	+0.628	12.354	+0.628
			12.4	+0.849	12.45	+0.546		
			12.5	+0.401	12.34	+0.851		
X_3	13	−0.024	13.2	−0.828	13.24	−0.443	13.245	−0.582
			13.4	+0.433	13.45	−0.484		
			13.5	−0.802	13.25	−0.862		
X_4	14	−0.211	14.2	−0.790	14.23	−0.196	14.235	−0.055
			14.3	−0.472	14.35	−0.058		
			14.5	−0.732	14.25	−0.782		
X_5	15	+0.437	15.2	−0.206	15.23	+0.463	15.234	+0.431
			15.3	+0.843	15.34	+0.794		
			15.4	+0.779	15.24	+0.107		
	23	+0.774	23.1	+0.935	23.15	+0.529	23.145	+0.369
	24	+0.598	24.3	−0.441	24.35	−0.026	24.135	+0.014
	25	+0.929	25.1	+0.915	25.14	+0.680	25.134	+0.263
	34	+0.917	34.2	+0.895	34.25	+0.893	34.125	+0.694
	35	+0.840	35.1	+0.946	35.14	+0.805	35.124	+0.624
	45	+0.656	45.2	+0.338	45.23	−0.324	45.123	−0.268

[a] Table II gives values of the variates in the states included in the calculations.

[b] 5% level of significance: zero order 0.396, third order 0.423.

One can use this regression equation nonetheless to arrive at certain tentative conclusions. For example, if X_1 be assumed to be zero, proper values substituted for X_3, X_4, and X_5, and the equation solved for X_2, it appears that average farmers will not use any commercial nitrogen on soils containing 0.10, 0.15, 0.20, and 0.25% nitrogen unless the value of the crop to be grown on them exceeds about 10, 20, 30, and 40 dollars per acre, respec-

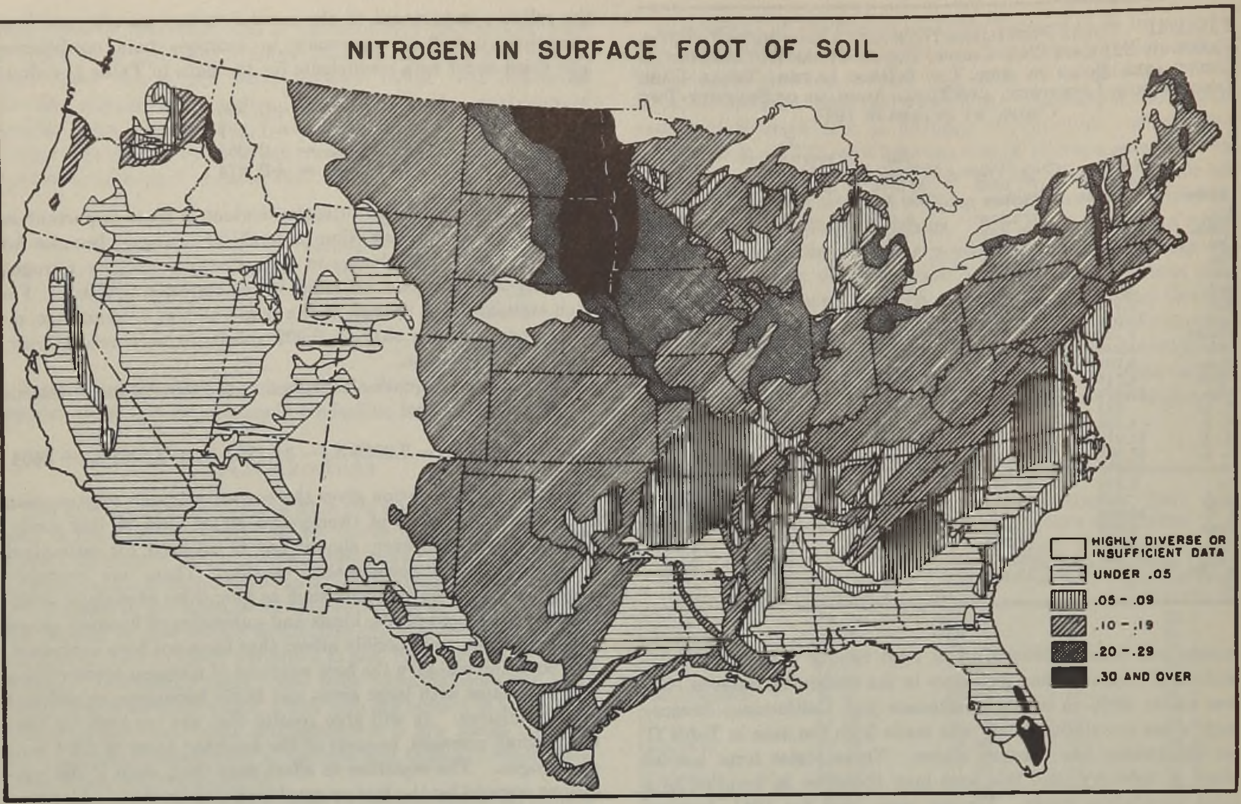

Figure 2. Soil Nitrogen Map of the United States

tively. If it be assumed that average conditions in the East would apply approximately in other states, it is clear from Table I that nitrogen will never be consumed in large quantities in Minnesota, Iowa, Kansas, North Dakota, South Dakota, or Nebraska as long as the acre values of the crops usually grown there remain as low as they have been in the past. On the other hand, greatly increased consumption of nitrogen appears probable for California, Arizona, Oregon, Washington, Utah, and Idaho.

SEASONAL FACTORS

The principal factors apparently causing variations from year to year in nitrogen consumption are the farm income in the previous year, the prospects of income in the present year, the proportion of last year's income left after expenses are paid, and the relative cost of a unit of fertilizer nitrogen.

Another paper (*15*) showed that there is a high degree of association between the amount of money spent by farmers for all fertilizers and their income from sale of crops and government payments. The principal correlation coefficients obtained in that study are given in Table IV. The multiple correlation between these three factors combined and expenditures for fertilizers is 0.968. Thus, about 93% of all the deviations from the mean quantity of money spent for fertilizers in the years from 1911 to 1943 is accompanied by corresponding deviations in the three factors mentioned above. It should be noted, however, that this correlation is between income and money spent for all fertilizers and not between income and tons of nitrogen consumed.

The wholesale prices of nitrogenous fertilizer materials have changed with reference to those for phosphates and potash salts with the passage of time. This has resulted in a shift in the proportions of the three primary plant nutrients consumed. Table V shows the proportion of the sum of these three represented by nitrogen. From 1880 to about 1910 the price of nitrogen increased relative to prices of P_2O_5 and K_2O, and the proportion of nitrogen to total nutrients consumed decreased both in mixed fertilizers and all fertilizers. Since then nitrogen has become relatively cheaper and the proportion of nitrogen has gone up. But the proportion used as separate materials has gone up faster than that used as mixed fertilizers. Shaw, Ezekiel, and Parker (*21*) studied the relation between proportion of nitrogen to phos-

Table IV. Association between Expenditures for Fertilizers and Factors Affecting Them, 1911 to 1943, Inclusive (*15*).

Factor	Zero-Order Coefficient	Second-Order Coefficient
Income from sale of crops and govt. payments in previous year	+0.929	+0.781
Income from these sources in same year	+0.901	+0.554
Proportion of previous year's income left after expense deduction	+0.570	+0.305
5% level of significance	0.344	0.355
1% level of significance	0.443	0.456

Table V. Proportion of Nitrogen to Total Plant Nutrients in Mixed Fertilizers and in All Fertilizers Consumed in U. S. by Years

Year	Fertilizers, %		Year	Fertilizers, %	
	Mixed	All		Mixed	All
1880	17.78	18.46	1931	17.78	25.36
1890	16.79	18.50	1932	18.23	26.11
1900	14.39	15.70	1933	18.78	25.94
1910	14.19	16.13	1934	19.61	25.79
1920	16.55	19.89	1935	19.05	25.63
1925	15.63	22.46	1936	19.42	25.79
1926	15.66	22.39	1937	19.51	25.68
1927	16.17	23.14	1938	19.35	25.81
1928	16.37	23.57	1939	19.33	25.93
1929	17.05	24.05	1940	19.19	26.48
1930	17.32	24.72	1941	18.92	26.76

TABLE VI. RELATIVE PRICE PER UNIT OF NITROGEN IN VARIOUS FORMS AND PERCENTAGES OF TOTAL FERTILIZER NITROGEN CONSUMED IN THESE FORMS IN MANUFACTURING COMMERCIAL MIXED FERTILIZERS AND AS SEPARATE MATERIALS DIRECTLY IN AGRICULTURE, BY YEARS

	Solid Nitrates			Solid Ammonium Salts			Natural Organics			Synthetic Organics			Ammonia and Its Solns.			Total N	
Year	Relative price	Mixed, %	Separate, %	Relative price	Mixed, %	Separate, %	Relative price	Mixed, %	Separate, %	Relative price	Mixed, %	Separate, %	Relative price	Mixed, %	Separate, %	Mixed, %	Separate, %
1880	107.2	0.9	1.4	104.1	1.3	0.9	88.8	42.4	53.1	...	...	...	..	..	...	44.6	55.4
1890	87.7	2.9	2.6	119.7	0.4	0.2	92.6	42.7	51.2	...	...	...	..	..	...	46.0	54.0
1900	92.0	3.4	7.7	108.3	1.0	0.4	99.7	44.9	42.6	...	...	...	..	..	...	49.3	50.7
1910	88.7	7.1	17.0	84.9	8.0	13.4	116.7	33.6	20.2	109.6	0.9	...	..	..	...	49.6	50.4
1920	86.2	8.1	16.9	79.2	9.8	30.1	169.0	22.0	11.8	65.6	1.1	0.2	..	..	...	41.0	59.0
1925	100.9	10.3	28.8	81.5	13.2	17.7	150.2	16.5	8.9	67.4	4.7	0.1	..	..	...	44.7	55.3
1926	103.9	8.2	26.4	80.1	16.8	19.6	146.8	15.4	8.4	69.3	4.9	0.3	..	..	...	45.3	54.7
1927	100.6	5.8	26.5	72.8	22.1	18.0	164.1	12.1	11.2	62.5	5.0	0.4	..	..	...	45.0	55.0
1928	98.2	5.9	27.1	77.4	21.2	22.4	208.9	11.4	5.6	63.1	5.0	0.6	52.5	1.0	...	44.5	55.5
1929	164.0	5.6	27.1	75.2	20.7	18.7	195.2	10.3	6.3	71.1	4.2	1.4	54.6	5.7	...	46.5	53.5
1930	104.3	5.0	25.3	75.0	20.5	19.4	188.4	9.5	6.5	73.7	3.7	2.4	58.6	7.6	...	46.3	53.7
1931	124.5	4.6	23.5	70.7	22.7	17.7	152.9	8.8	11.1	80.7	3.9	1.1	71.2	6.6	...	46.6	53.4
1932	130.8	4.0	13.7	71.7	24.3	25.9	128.7	9.8	15.3	77.4	4.0	0.9	91.4	6.1	...	48.2	51.8
1933	102.4	3.5	15.8	75.0	26.7	22.7	176.7	10.3	10.6	75.0	4.0	0.8	70.0	5.6	...	50.1	49.9
1934	93.2	4.3	19.3	71.4	26.6	18.1	206.4	10.4	8.5	67.2	3.9	2.0	61.7	7.6	...	52.8	47.2
1935	89.1	4.7	26.7	68.5	26.3	11.6	204.8	9.6	7.1	72.7	3.7	2.5	64.8	7.8	...	52.1	47.9
1936	91.0	4.6	30.5	68.7	27.2	6.5	206.6	8.5	8.1	72.2	3.4	2.6	61.6	8.2	0.2	51.9	48.1
1937	81.8	4.2	32.3	65.9	28.3	6.5	224.1	7.2	5.2	69.9	3.8	3.0	58.4	8.7	0.7	52.3	47.7
1938	92.0	4.3	30.1	74.5	24.7	9.9	192.8	7.4	5.4	73.9	4.3	2.2	66.8	10.9	0.8	51.6	48.4
1939	96.6	4.5	29.3	71.6	23.3	10.5	200.6	8.0	4.3	71.2	4.7	2.5	65.8	12.0	0.9	52.5	47.5
1940	91.6	4.8	27.4	74.6	20.1	14.5	193.6	7.6	4.0	73.6	4.5	3.5	66.5	12.4	1.2	49.4	50.6
1941	86.3	3.5	28.1	72.0	17.5	15.0	206.8	7.7	2.9	72.5	4.5	4.3	62.3	16.1	0.4	49.3	50.7
1942	79.7	4.3	22.0	67.5	28.6	15.0	221.7	8.3	2.7	73.6	3.3	0.7	57.5	14.4	0.7	58.9	41.1
r*		−0.0491	−0.1828		−0.9134	−0.5598		−0.8633	−0.8567		−0.6036	−0.2477		−0.1456	−0.007		

* r = correlation coefficient between relative price and percentage of total consumption in this form.

phoric acid and potash and changes in the wholesale prices of each. They developed an equation which seems to prove that the changes in proportions that have occurred from 1926 to 1941 were due almost entirely to changes in the relative wholesale cost per unit of nitrogen as compared with costs of phosphoric acid and potash.

Total plant food, as well as nitrogen consumption on a tonnage basis per unit of farm income, is going up with the passage of time in spite of the fact that the total expenditure for fertilizers has remained for many years almost a constant percentage of farm income. A part of this increase is due to decreased nitrogen prices, but the principal reason is that the total plant-food content of fertilizers has increased. For example, the sum of the nitrogen, phosphoric acid, and potash contents has gone up from 17% in 1926 to 20% in 1941. This increase of concentration has made possible the use of relatively more fertilizer without the corresponding reduction in either wholesale or retail price, because of savings in bags, freight, and handling costs. In other words, the farmer has spent no more money, but a larger proportion of his money has gone for fertilizer and less for freight and other items. Shaw, Ezekiel, and Parker (*21*) developed an equation which shows this trend toward higher concentration mathematically; they calculated that a 20% reduction in wholesale prices of nitrogen, phosphoric acid, and potash would increase consumption of each 11.4%. On the other hand, a 20% increase in the total plant-food content of fertilizers would automatically increase the consumption of nitrogen, phosphoric acid, and potash approximately 10% each. Thus, a 20% increase in the average grade of fertilizers would do about as much to increase consumption of nitrogen as a 20% reduction in price. There is little likelihood that prices of fertilizers will be reduced 20% in the near future, but it should not be too difficult to increase the average grade of fertilizers from a total nitrogen, phosphoric acid, and potash content of 20 to 24%.

The 20% increase in plant-nutrient content in the past fifteen years has been due to research, technological advances, and an educational campaign by the industry and governmental agencies. In this indirect way research and education have influenced to a considerable extent the total consumption of nitrogen. Education and salesmanship have had some direct effect also on total consumption because increased usage results in increased income and this, in turn, tends to maintain usage on a higher level.

KIND OF NITROGEN

Fertilizer nitrogen is derived from a great variety of materials, which have different properties and contain the nitrogen in several kinds of chemical combination. For some uses all forms of fertilizer nitrogen are directly competitive, but for others they are not. In other words, there are limitations on the kind or quantities of some materials that may be used under certain conditions.

The factors that influence the proportions of the various kinds of nitrogen consumed are: relative price, chemical properties, physical properties, effects on the soil, and salesmanship. All of these are important, and their effects are too complicated and interrelated for complete treatment here. The most important factor under ordinary circumstances is the relative price of the various forms. This was studied somewhat, and a few resulting conclusions are given.

For convenience in studying the effects of price, the different forms of nitrogen are grouped into the following classes: natural organic, solid ammonia, solid nitrate, synthetic organic, and solution. Table VI gives the proportion of each used, in comparison with price relative to the average price of all forms of nitrogen in that year. The average price of the five forms is taken as 100. The correlation between the percentage of total consumption and the relative price was calculated with figures for all the years shown except 1942. The latter year was excluded from the calculations because buyers did not have a free choice in that year. The coefficients are given at the bottom of the columns to which they apply. These coefficients do not measure the correlation between total usage of each form in comparison with price, but rather the shifts in usage of the same form with shifts in relative price.

Obviously, if price were the only consideration, all of the consumption after a few years should consist of the cheapest form. But the cheapest form in one area is not necessarily the cheapest in other parts of the United States. Nevertheless, the relations shown in Table VI are believed to be those that affected the majority of fertilizer users.

The correlation coefficients indicate that price changes have been an important factor in causing shifts in the relative proportions of the natural organic, synthetic organic, and solid ammonia forms. The price of a unit of nitrogen in the natural organics up to about thirty years ago was as cheap as, or cheaper than, that of a unit in chemical forms. In recent years the price of natural organic nitrogen has been extremely high in proportion to chemical forms, and as a consequence the consumption of this form has been dropping. Shaw, Ezekiel, and Parker (*21*) developed a formula which indicates that, as the cost of insoluble nitrogen goes up, the proportion used drops, but that even at very high prices a little would still be used for conditioning effects. This has been the case in the past. It is always possible, however, that granulation or other means of improving the physical properties of fertilizers will upset this relation in the future.

The coefficients for solid nitrate forms do not indicate much effect on consumption from price changes. This is not quite true, because other factors are playing a part in this case. Up to 1942 solid nitrate forms consisted largely of sodium nitrate and for present purposes may be considered to be sodium nitrate. Since 1930 the relative price of this material has declined, but nevertheless its usage in mixed fertilizers has also dropped. This drop wiped out the high correlation that would otherwise have existed. It was due to substitution by ammonium nitrate and other forms of nitrogen in solution at a still lower price.

The correlation in the case of side-dressing sodium nitrate is −0.1828. It seems that the use of this material increased more than could be expected solely from price considerations between 1920 and 1930. This was due partly to a widespread educational program. When the correlation is calculated separately for the two periods 1880 to 1920 and 1925 to 1941, the coefficients are −0.6221 and −0.6603. Thus, it seems fair to conclude that about half of the changes in usage within these two periods may be ascribed solely to changes in price in the opposite direction relative to those of other nitrogenous materials.

The coefficients indicate little correlation between usage of solutions and shifts in price. This is easily explained, however. Liquid ammonia has been the cheapest form of fertilizer nitrogen from the beginning of its use in 1928, except in 1932. During the first two years of its use it was cheaper relatively than at any time since, and naturally the proportion of the total was small at first. This usage has grown steadily, however, until in 1941 and 1943 about two thirds of the total quantity that could be efficiently utilized in making mixed fertilizers has been so used. Since the proportion that can be used is limited to about 40 pounds of free ammonia per 1000 pounds of superphosphate in the mixture, it would be fairer to calculate the correlation with the proportion of the potential use. This was done leaving out the figures for 1928 and 1929. In this case the coefficient is −0.392. This shows, then, that shifts in price relative to other forms of nitrogen were followed by shifts in consumption in the opposite direction to the extent of about 15% of the total changes in usage over the entire period.

It has been shown that research and education, including salesmanship, have been important factors in the kind of nitrogen used in agriculture, even though these factors appear to have had little effect upon the total amount of money the farmer has spent for fertilizer nitrogen. Fluctuations in total expenditures can be largely accounted for by changes in farm income and price considerations. This is not true, however, of changes in the kind of nitrogen used.

SUMMARY

Total consumption of fertilizer nitrogen varies in rate from place to place. It also varies in the same place from year to year. The principal factors influencing rate of consumption in any given state are the comparative value of crops per acre of cultivated land and the nitrogen content of the soil. The net correlation between rate of nitrogen consumption in twenty-five states in the eastern half of the United States and value of crops in 1941 is +0.628 and with soil nitrogen content is −0.582. The multiple correlation is 0.909. The most important factor is the nitrogen content of the soil, followed by the value of crops produced per acre and the income from livestock, as shown by beta coefficients of −1.237, +0.909, and −0.063, respectively. The regression equation indicates that the use of commercial nitrogen will remain very low in Minnesota, Iowa, the Dakotas, Nebraska, and Kansas as long as the per acre values of crops grown there remain as low as they have been in the past. Increased consumption of nitrogen in the future is forecast for the Pacific Coast states and some of the Intermountain states.

The principal factors causing variations in consumption in the same area from time to time are farm income in the previous year, prospects for income in the same year, proportion of the previous year's income left over after all expenses of production have been paid, and prices of nitrogen, phosphoric acid, and potash. The relative importance of these factors is in the order named.

Consumption of plant nutrients, including nitrogen, is increasing independently of farm income or price. This increase is due to raising the total plant-food content of fertilizers. A 20% increase in the average plant-food content stimulates consumption as much as a 20% drop in price.

The most important factors affecting the form of nitrogen employed for various fertilizer uses are chemical and physical properties of the various materials available, price per unit of nitrogen in competing forms, their effects on the soil, and research and education, including sales promotion.

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The author is grateful to C. P. Barnes, of the Division of Soil Survey, who estimated the average nitrogen content of the soils for each state from the soil series data assembled in this study and assisted in preparing the soil nitrogen map, and to Mildred Drain who checked the calculations.

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d-Isoascorbic Acid as an Antioxidant

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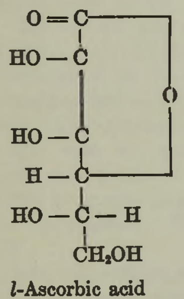
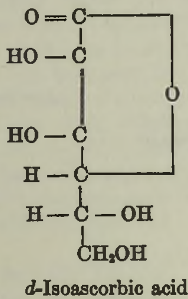
As previously reported, *d*-isoascorbic acid possesses significant antioxidant properties toward *l*-ascorbic acid (vitamin C) in pure solutions. These findings have been reaffirmed by oxidation-reduction potential studies which show that *d*-isoascorbic acid would be expected to oxidize more rapidly than *l*-ascorbic acid in food products. The addition to 30 mg. of *d*-isoascorbic acid per pint to bottled tomato juice is effective in preventing loss of natural *l*-ascorbic acid during storage, even under adverse conditions. The added *d*-isoascorbic acid is also effective in preventing deleterious color and flavor changes in juice stored for 5 months at 49° C. (120° F.). The addition of larger amounts of *d*-isoascorbic acid to tomato juice causes a flavor change more characteristic of uncooked tomato juice than the heated and processed product. It appears that *d*-isoascorbic acid may prove to be of value in stabilizing the color, flavor, and ascorbic acid (vitamin C) content of processed fruit juices and other foods.

A PREVIOUS report from this laboratory (*16*) indicated that *d*-isoascorbic acid oxidized more rapidly than *l*-ascorbic acid in a buffered aqueous solution. The purpose of the present investigation was to apply those findings (*16*) on a practical basis and ascertain whether *d*-isoascorbic acid functions as an antioxidant towards natural and added *l*-ascorbic acid in such products as processed tomato juice and grape juice.

d-Isoascorbic acid (*d*-araboascorbic acid) differs from *l*-ascorbic acid only in the relative position of the hydrogen and hydroxyl groups in the fifth carbon atom of the molecule:



l-Ascorbic acid



d-Isoascorbic acid

The antiscorbutic activity of *d*-isoascorbic acid is only about one twentieth that of *l*-ascorbic acid (*16, 17*).

The use of *l*-ascorbic acid and its analogs has been suggested (*5–8*) as a means of preventing darkening, flavor changes, and rancidity in such products as beer, oil emulsions, and other foods. The addition of small amounts of *l*-ascorbic, *d*-isoascorbic, or *d*-glucoascorbic acid to glass- and tin-packed foods naturally low in vitamin C has been found effective (*4*) in controlling discoloration and undesirable flavor changes. The development of off-flavors in bottled orange juice was delayed by the addition of *l*-ascorbic, *d*-isoascorbic, or *d*-glucoascorbic acid (*12*). However, the addition of these ascorbic acids did not prevent darkening of the juice. *d*-Isoascorbic acid compared favorably with other antioxidants in stabilizing the flavor in canned orange juice (*13*).

Greenbank (*9*) found that oxidized flavor develops in milk when its oxidation-reduction potential rises; the addition of *l*-ascorbic acid to milk prevents the development of oxidized flavor. In studies on the oxidation rate of *l*-ascorbic acid and its analogs, Johnson and Zilva (*10*) found that *d*-isoascorbic acid was oxidized at a velocity similar to that of *l*-ascorbic acid by cucumber ascorbic acid oxidase; ascorbic acids with the lactone ring to the right oxidized at a much faster rate than their antimorphs. The addition of ascorbic acid to true-fruit orange and grapefruit beverages, in excess of that required to take up the free oxygen in the container, distinctly increased the period of retention of the normal taste and flavor (*15*). It has been pointed out (*8*) that the development of pasteurized taste and the formation of the so-called oxidation haze in ales and beers are inhibited by the addition of ascorbic acid compounds. The use of the fatty acid mono esters of *l*-ascorbic and *d*-isoascorbic acids has been found to be effective in preventing or retarding rancidity in fats such as lard (*14*).

Beattie, Wheeler, and Pederson (*1*) found that there is a progressive loss in ascorbic acid content and red color during the storage of strawberry juice. When *l*-ascorbic acid or *d*-isoascorbic acid was added, a more rapid reduction in red and yellow color occurred, the red color was less intense when the rate of

Table I. Effect of Added *d*-Isoascorbic Acid on Changes in *l*-Ascorbic Acid, Color, and Flavor in Bottled Tomato Juice during Storage

		Original Ascorbic Acid Content, Mg./100 Ml.			7-Month Storage at Room Temperature						5-Month Storage at 49° C.					
Sample No.	*d*-Isoascorbic Acid Added, Mg/ Bottle	Total	*l*-Ascorbic	*d*-Isoascorbic	Total ascorbic, mg./100 ml.	*l*-Ascorbic, mg./100 ml.	*d*-Isoascorbic, mg./100 ml.	Loss of *l*-ascorbic, %	Flavor	Color	Total ascorbic, mg./100 ml.	*l*-Ascorbic, mg./100 ml.	*d*-Isoascorbic, mg./100 ml.	Loss of *l*-ascorbic, %	Flavor	Color
1	0.0	21.0	21.0	0.0	15.5	15.5	0.0	26.0	Good	Good	16.0	16.0	0.0	23.8	Off	Browned
2	30.0	27.0	21.0	6.0	21.0	21.0	0.0	0.0	Good	Good	19.0	19.0	0.0	10.5	Good	Good
3	95.0	39.0	21.0	18.0	28.6	21.0	7.6	0.0	Fresh	Good	23.0	21.0	2.0	0.0	Fresh	Good

destruction leveled off, the increase in yellow following an original decrease was slower, and the amount of ascorbic acid lost was considerably greater. It was suggested that, since ascorbic acid is oxidizable and pigments are reducible, they may react with each other. Increasing the concentration of ascorbic acid increased the rate of change of color as well as the rate of loss of ascorbic acid.

To gain an insight into the mechanism by which *d*-isoascorbic acid functions as an antioxidant toward *l*-ascorbic acid, oxidation-reduction studies were undertaken. The redox potentials were determined potentiometrically. A laboratory Model G Beckman pH meter, equipped with saturated calomel and platinum electrodes, was used as the potentiometer. Potassium dichromate (0.1 *N*) was the oxidizing agent. All titrations were carried out under carbon dioxide.

The redox studies revealed a slight difference in the respective rates of oxidation of *d*-isoascorbic and *l*-ascorbic acids (Figure 1). Each curve is the average of four determinations. The ascorbic acids were at a concentration of 0.5 mg. per ml. in a citrate buffer medium adjusted to pH 4.05. This difference might not seem significant from the curves themselves, but previous studies and the applied aspects of this study demonstrate that the slightly greater reducing characteristics of *d*-isoascorbic acid permits it to be an antioxidant for *l*-ascorbic acid.

TOMATO JUICE

To determine whether added *d*-isoascorbic acid would prevent the oxidation of the *l*-ascorbic acid naturally present in processed tomato juice, experimental packs of the product were prepared and stored at two different temperatures. Juice from fresh ripe tomatoes was prepared by the hot break method and put through a stainless steel cyclone-type juicer. The warm juice was heated to 88-90° C. in a stainless steel steam-jacketed kettle and filled immediately into preheated pint glass bottles, leaving a sufficient head space for expansion of the product during processing. The bottles were sealed immediately with crown-type caps with glazed paper liners. The bottled juice was processed for 30 minutes in boiling water and cooled. Where *d*-isoascorbic acid was added, weighed amounts were placed in the bottles just prior to filling (Table I).

After processing, half the bottles of each group were stored in cartons for 5 months at 49° C., a severe storage condition. The remaining bottles were stored in cartons at room temperature (23.9-26.7° C.) for 7 months.

Ascorbic Acid. Determinations were made by the 2,6-dichlorobenzenone indophenol dye titration method (*11*) on the fresh tomatoes and the juice prior to bottling. The ascorbic acid content of the three lots of juice was determined immediately after processing. The results from three different bottles, which showed only a slight variation, were averaged.

At the end of 5-month storage at 49° C. the total reduced ascorbic acid content of the tomato juice samples was determined by the dye titration method. This chemical method indicated both the *l*-ascorbic and the *d*-isoascorbic acid. The amount of biologically active *l*-ascorbic acid in the samples was determined by the 25-day weight response bioassay method (*3*). In the amounts used, the *d*-isoascorbic acid would have little influence on the response of the guinea pigs in the bioassay method. The amount of *d*-isoascorbic acid present was taken as the difference between the total ascorbic acid content, determined by the dye method, and the biologically active ascorbic acid. After 7 months the tomato juice stored at room temperature was tested for ascorbic acid content by the same method.

As Table I shows, the addition of *d*-isoascorbic acid to bottled tomato juice was quite effective in preventing a loss of natural *l*-ascorbic acid present. This was true even when the juice was stored at 49° C. It would appear that the protective action of *d*-isoascorbic acid could be attributed to the fact that, in processed tomato juice, it oxidized more readily than the *l*-ascorbic acid.

The addition of *d*-isoascorbic acid was also effective in preventing undesirable color changes in tomato juice stored at 49° C. This severe storage condition caused a definite browning in the control bottles, but the addition of either 30 or 95 mg. of *d*-isoascorbic acid per pint bottle prevented this discoloration.

Of particular interest was the effect of adding *d*-isoascorbic acid on the flavor of tomato juice. During storage at 49° C. the control lot of juice developed a definite off-flavor, whereas that to which 30 mg. per pint of *d*-isoascorbic acid was added main-

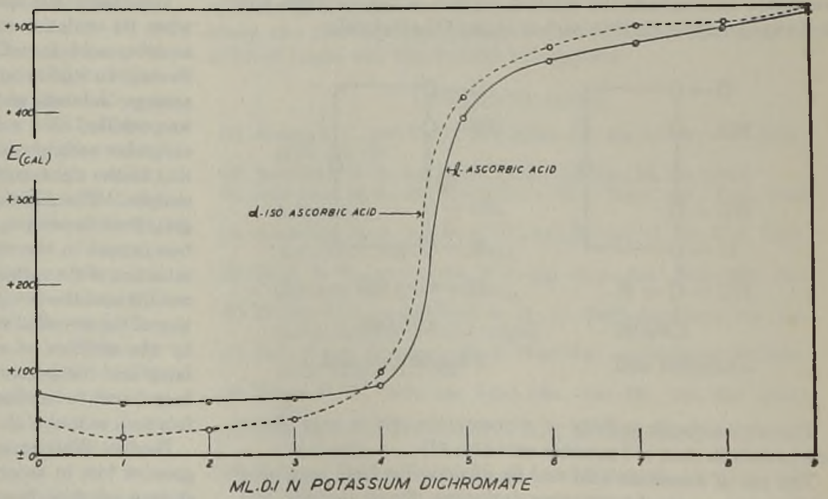


Figure 1. Comparative Oxidation Curves of *l*-Ascorbic and *d*-Isoascorbic Acids at Concentration of 0.5 Mg. per Ml. in Citrate Buffer of pH 4.05

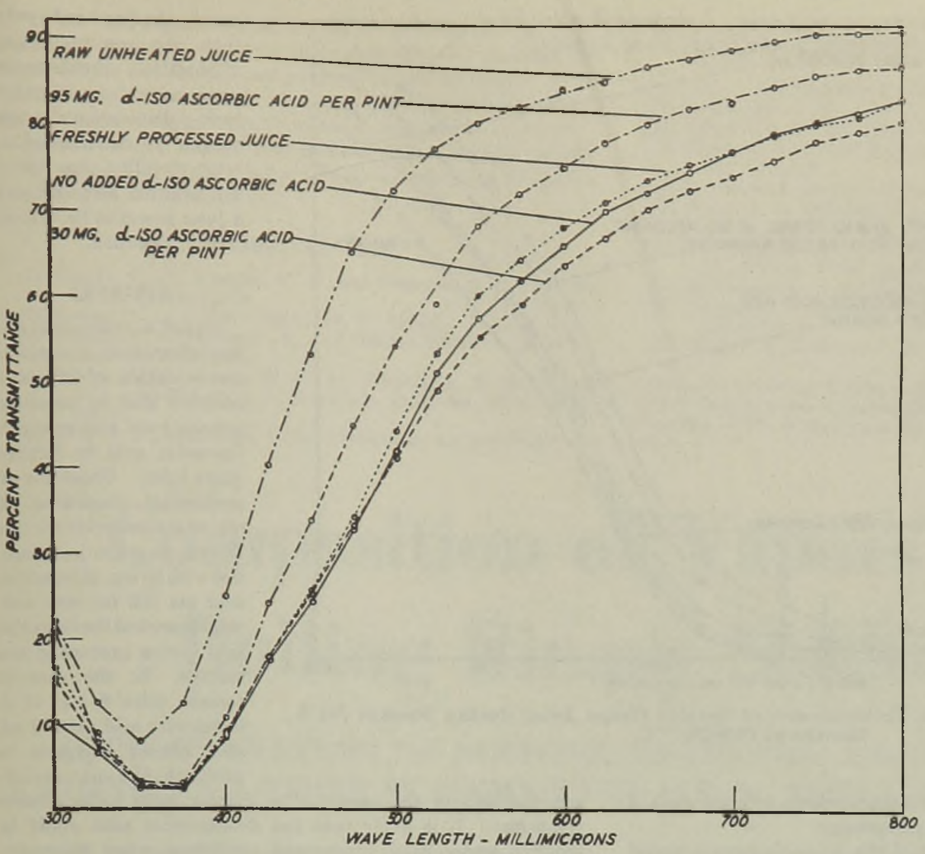


Figure 2. Effect of Added *d*-Isoascorbic Acid on Light Transmission of Serum from Tomato Juice Stored 11 Months at 23.9–26.7° C.

tained its original good flavor. The juice containing 95 mg. of *d*-isoascorbic acid per pint bottle was not like regular processed tomato juice in flavor but rather tended to resemble more nearly fresh unheated tomato juice. For lack of a better term this flavor has been described as "fresh". Juice with this amount of added *d*-isoascorbic acid stored both at 49° C. and at room temperature had this fresh flavor. Such juice was not so palatable as ordinary juice because the so-called fresh flavor resulted in a somewhat insipid and seemingly light-bodied product.

Color. To obtain further information on the influence of added *d*-isoascorbic acid on the color of processed tomato juice, light transmission curves of undiluted tomato juice serum were made. The tomato juice samples were centrifuged for 10 minutes at 5000 r.p.m. and the clear serum was decanted off. The light transmission of the serum was measured over the wave length range of 300 to 800 millimicrons in a Coleman Model 11 Universal spectrophotometer. Data were obtained on the serum from fresh raw unheated tomato juice, glass-packed tomato juice shortly after it was processed, and the three experimental lots of tomato juice after 11-month storage at room temperature. The results are shown in Figure 2.

The light transmission curves show that the heat treatment to which tomato juice is subjected during preparation and processing intensifies the color throughout the wave length range of 300 to 800 millimicrons. This is particularly true in the spectral region between 450 and 650 millimicrons. There was little or no difference in the light transmission characteristics of the control tomato juice and that with 30 mg. of added *d*-isoascorbic acid stored for 11 months as compared with freshly packed tomato juice. However, the juice to which 95 mg. of *d*-isoascorbic acid were added per pint bottle had a significantly different light transmission curve in that the serum was lighter in color than the other samples which had been heated or stored. Its light transmission characteristics were more like that of raw tomato juice than were those of the processed samples. This fact, plus the fresh-like flavor of the juice to which the larger amount of *d*-isoascorbic acid was added, leads us to believe that the addition of a relatively large amount of *d*-isoascorbic acid to processed tomato juice tends to preserve the fresh characteristics by preventing changes which normally occur during heating. This property is undoubtedly due to the reducing action of ascorbic acid. Although comparable data are not available, one might expect that adding similar amounts of *l*-ascorbic acid to tomato juice would produce similar results.

GRAPE JUICE

To study the antioxidant effect of *d*-isoascorbic acid toward *l*-ascorbic acid when added to a food product, an experimental pack of grape juice was made in the usual manner; it was held for several months to allow the tartrates to settle out. The juice was then divided into three samples, with ascorbic acid added as shown in Table II.

Each lot was then flash-pasteurized in a block tin coil to a temperature of 82–85° C. and filled immediately into preheated pint bottles. The bottles were filled and sealed with crown caps with glazed paper liners. The bottles were placed on their sides and cooled under a fine cold water spray. Samples of the three lots of grape juice were taken immediately for ascorbic acid and light transmission tests. The remaining bottles were stored in cartons at 23.9–26.7° C. for 8 months.

The juice was diluted 3:1 before its light transmission characteristics were determined in order to bring the percentage transmission onto a sensitive portion of the galvanometer. The ascor-

Table II. Effect of *d*-Isoascorbic Acid on Stability of Added *l*-Ascorbic Acid Color and Flavor in Bottled Grape Juice during Processing and Storage

Sample No.	Original Ascorbic Acid Content, Mg./100 Ml.			8-Month Storage at 23.9–26.7° C.					
	Total	*l*-Ascorbic	*d*-Isoascorbic	Total ascorbic, mg./100 ml.	*l*-Ascorbic, mg./100 ml.	*d*-Isoascorbic, mg./100 ml.	Loss of *l*-ascorbic, %	Flavor	Color
1	0.0	0.0	0.0	0.0	0.0	0.0	..	Good	Good
2	50.0	50.0	0.0	36.0	36.0	0.0	28.0	Good	Good
3	70.0	50.0	20.0	51.0	50.0	1.0	0.0	Good	Good

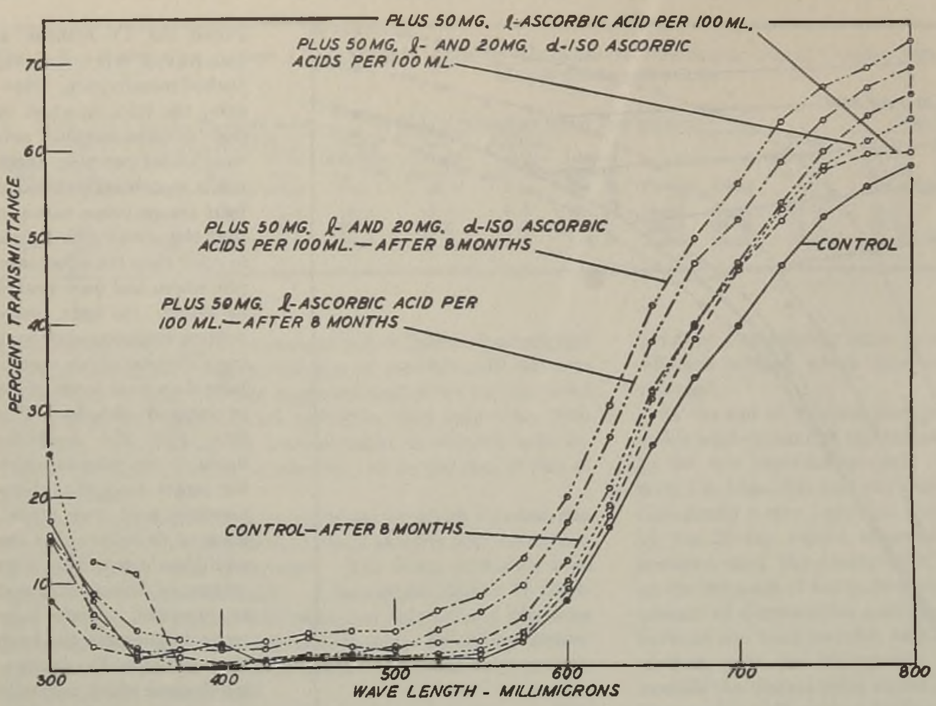


Figure 3. Change in Light Transmission of Bottled Grape Juice during Storage for 8 Months at 23.9–26.7° C.

bic acid determinations were made in accordance with the method of Bessey (*2*), using an Evelyn photometer.

Ascorbic Acid. At the end of the 8-month storage period the total ascorbic acid contents of the grape juice samples was determined. As with the tomato juice, the chemical method could not be used to differentiate between the added *l*-ascorbic acid and the *d*-isoascorbic acid; consequently the 25-day weight response bioassay method was again used to determine the respective percentages of *d*-isoascorbic and *l*-ascorbic acid retained. The ascorbic acid content was determined chemically every other day on fresh bottles of juice which were then held under refrigeration for 1 day. The guinea pigs were fed on the basis of the chemical determination.

As Table II shows, *d*-isoascorbic acid protected *l*-ascorbic acid from oxidation. Although there was a 28% loss of *l*-ascorbic acid in the bottles to which only 0.5 mg. of *l*-ascorbic acid was added per ml., no loss of that 0.5 mg. ascorbic acid occurred, provided 0.2 mg. of *d*-isoascorbic acid per ml. was also added. This study on grape juice reaffirms the work on tomato juice that *d*-isoascorbic acid is an antioxidant for *l*-ascorbic acid.

Color. As with the tomato juice, the question arises as to the effect of *d*-isoascorbic acid on color changes. Since the color changes in tomato juice are oxidative, the use of *d*-isoascorbic acid with its reducing action is highly desirable. But that same reducing tendency in pigmented juice might be considered detrimental to the quality of the juice from the point of view of color, on the basis that anthocyanin pigments are reduced easily with concomitant color changes. Figure 3 shows that the addition of ascorbic acid to the grape juice produced fading at the red end of the spectrum in proportion to the initial concentration of ascorbic acid immediately after processing and at the end of the storage period. However, it would not appear that the addition of *d*-isoascorbic acid as an antioxidant or *l*-ascorbic acid for fortification to grape juice would be objectionable on the grounds that ascorbic acid produces fading. As a matter of fact, the grape juice to which the ascorbic acids were added had a somewhat more pleasing red color than the control group of bottles. Furthermore, since several investigators have demonstrated that oxygen is detrimental to color stability, the use of the ascorbic acids in such a juice seems to be without serious objection.

SUMMARY

Added *d*-isoascorbic acid was effective in preventing the oxidation of natural *l*-ascorbic acid in processed tomato juice and synthetic *l*-ascorbic acid in fortified grape juice. Under the experimental conditions 20 mg. of *d*-isoascorbic acid per 100 ml. in grape juice fortified with 50 mg. of *l*-ascorbic acid per 100 ml. was sufficient to protect the *l*-ascorbic acid during processing and storage. In the case of tomato juice 6 mg. of *d*-isoascorbic acid per 100 ml. was almost adequate to protect the natural *l*-ascorbic acid in the juice during storage, even under adverse conditions. It is likely that less *d*-isoascorbic acid would be required under good commercial conditions when incorporation of air into the product during processing and packaging can be kept at a minimum. In such products as grape juice fortified with vitamin C or tomato juice, added *d*-isoascorbic acid appears to protect the *l*-ascorbic acid by being preferentially oxidized.

With tomato juice the addition of *d*-isoascorbic acid in amounts sufficient to protect the *l*-ascorbic acid was also effective in preventing deleterious changes in color and flavor which occur during storage at high temperatures. The addition of either *d*-iso- or *l*-ascorbic acid to grape juice appeared to have little effect on its flavor but did tend to reduce the intensity of the red color. However, this change in color was not apparent to the eye.

Of particular interest was the effect of adding 95 mg. of *d*-isoascorbic acid per pint of tomato juice. The resulting juice had a definite fresh flavor and resembled unprocessed juice which had been expressed from tomatoes by the hot-break method or raw juice, rather than what is normally considered to be good canned juice. This amount of added *d*-isoascorbic acid was apparently effective in preventing some of the flavor changes which occur on heating so that the processed juice tended to resemble fresh raw juice in flavor.

While the experimental work reported indicates the effectiveness of *d*-isoascorbic acid as an antioxidant in such products as tomato and fortified grape juice, it seems likely that it may also be used effectively in other fruit juices and concentrates. Our experience indicates that each product should be treated individually as regards the optimum amount of *d*-isoascorbic acid to be used. This will vary according to processing conditions, the end results desired, and the product in question. The use of *d*-isoascorbic acid is further complicated by the fact that no satisfactory quantitative chemical methods are available at present to differentiate between it and the biologically important *l*-ascorbic acid (vitamin C). Such other factors as availability, cost, labeling, and patents must also be considered.

It has been suggested that the use of *l*-ascorbic acid alone, in sufficient amounts, might be more desirable and practical for antioxidants and fortification purposes in food products. However, in products with delicate colors and flavors which are subject to oxidation changes during processing and storage, the use of *d*-isoascorbic acid may be more effective than *l*-ascorbic because of its apparently slightly faster rate of oxidation and its less intense degree of darkening (*16*).

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Composition of Vapors from Boiling Binary Solutions

AQUEOUS SYSTEMS OF ACETONE, METHANOL, AND METHYL ETHYL KETONE; AND OTHER SYSTEMS WITH ACETIC ACID AS ONE COMPONENT

Methods previously described have been utilized to determine the composition of vapors resulting from boiling solutions of binary liquids (vapor-liquid equilibrium data). Three binary systems have been studied at atmospheric and subatmospheric pressures. In each case water is one component and the second components are acetone, methanol, and methyl ethyl ketone. The data are correlated with one another and with published values by logarithmic plots; these plots are particularly applicable for evaluating and correlating data for several different temperatures or pressures. Other data at atmospheric pressure are presented for several binary systems, one component of which is acetic acid.

RECENT publications (*2, 5*) have described a simple and rapid method and apparatus for determining the equilibrium between a liquid solution and its vapors. The unit has been used for both binary and ternary solutions, under atmospheric pressure and vacuum. By taking data at several subatmospheric pressures, it is possible to plot the entire system of pressure, temperature, and compositions in both the liquid and vapor phases. Other relations which follow from these *p-t-x-y* data are activities, relative volatilities, and equilibrium constants; they also may be correlated as described by Othmer and Gilmont (*7*). The method and technique substantially as given in previous papers (*5, 6, 7*) were used to obtain and express the data presented here.

The correlation methods for the several properties were applied to the data; but only one type of plot is illustrated for the data of each system, and different plots are used for the different systems.

The experimental points are indicated in the vapor composition curves, the best smooth curve is drawn through them, and values of y at even values of x are picked off and tabulated. This smoothing is for convenience in using the data and is justified by the closeness of the experimental points to the curves. All of the materials were the purest commercially available and were then fractionated to recover substantially constant-boiling fractions.

SYSTEMS CONTAINING ACETIC ACID

Three binary systems containing acetic acid were studied at atmospheric pressure. The other liquids and their boiling points are: butyl Cellosolve acetate (ethylene glycol monobutyl ether acetate), 190° C.; methyl *n*-amyl ketone, 148.8° C.; methyl amyl acetate (methanol isobutyl carbinol acetate), 144.5° C. Data for these systems were taken at atmospheric pressure and are reported in Table I and Figure 1. Samples were analyzed at 18° C. with an Abbe refractometer; since refractive indices of these solutions have not been published, they are included in Table II.

SYSTEMS CONTAINING WATER

ACETONE. The vapor compositions of the system acetone-water were determined at 200, 350, 500, and 760 mm. pressure. These data are shown in Tables III and IV and Figure 2. Figure 3 is a log plot of vapor composition y *vs.* P, the total pressure at constant values of the liquid compositions. As previously sug-

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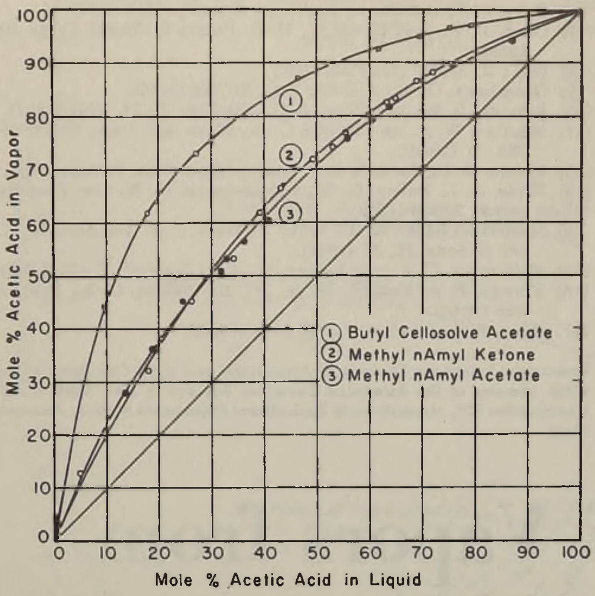

Figure 1. Vapor Compositions of Binary Systems Containing Acetic Acid as the Low-Boiling Component

Table I. Vapor Composition Data for Systems of Acetic Acid and High-Boiling Solvents[a]

Butyl Cellosolve Acetate			Methyl *n*-Amyl Ketone			Methyl *n*-Amyl Acetate		
Mole % HAc		Temp., ° C.	Mole % HAc		Temp., ° C.	Mole % HAc		Temp., ° C.
x	y		x	y		x	y	
			Experimental Data					
9.6	44.1	174.5	5.0	12.7	147.5	13.5	27.0	143.9
17.9	61.9	165.0	18.0	32.0	145.0	18.8	36.3	138.3
27.3	73.0	158.0	26.3	45.3	141.9	24.5	45.1	136.8
30.0	75.5	154.9	34.2	58.2	138.0	32.0	51.0	134.9
46.6	87.2	145.0	39.1	62.0	136.8	33.0	53.0	135.0
53.3	91.2	140.1	43.3	66.5	135.0	36.3	56.5	132.9
61.9	92.5	134.9	49.3	71.7	132.9	41.0	60.5	132.0
69.5	95.0	130.9	53.0	74.1	132.1	56.2	76.0	127.0
75.0	96.8	128.1	55.8	76.4	131.1	60.1	79.4	126.1
79.0	97.2	126.1	60.0	80.0	130.0	60.3	79.8	126.0
			63.4	82.7	129.1	63.9	81.9	125.1
			64.8	83.5	127.3	87.1	94.3	120.4
			68.7	86.7	126.5			
			72.0	88.2	125.8			
			75.7	89.9	124.5			
			Smoothed Data					
0	0	190.0	0	0	148.8	0	0	144.6
5	25.5	181.0	10	18.0	147.2	10	22.0	141.0
10	44.5	173.5	20	35.0	144.2	20	37.5	138.0
20	65.0	163.2	30	50.0	140.3	30	50.0	135.0
30	75.5	155.5	40	62.5	136.3	40	60.6	132.0
40	83.5	148.5	50	72.0	133.0	50	70.5	128.8
50	89.5	142.0	60	80.0	129.7	60	79.0	126.4
60	94.0	136.0	70	86.5	126.4	70	85.8	123.8
70	95.5	131.0	80	92.0	123.3	80	91.2	121.5
80	97.5	126.0	90	96.0	120.5	90	96.0	119.5
90	98.3	122.0	100	100.0	118.2	100	100.0	118.2
100	100.0	118.2						

[a] x = liquid, y = vapor.

gested (*7*), straight-line relations are obtained. Samples were analyzed by density in a 15-ml. pycnometer at 25° C.

Methanol. The same data were obtained for the system methanol-water at various subatmospheric pressures and also at atmospheric pressures as for acetone-water. Samples were analyzed by specific gravity at 20° C. Tables V and VI and Figure 4 present the vapor composition data in the familiar x-y form. The data of previous investigators (*1, 3*) at atmospheric pressure are compared in a (y-x) plot in the lower half. This plot serves as a good comparator of data since it tends to magnify differences. The present atmospheric data (which correlate well with the subatmospheric data) form a line as the mean of those of previous workers.

Samples were analyzed by specific gravity at 20° C. As a means of cross plotting to show the interrelation of pressure with these data, a logarithmic plot of the partial pressure of methanol, calculated from these data, against the vapor pressure of water as a reference substance is shown in Figure 5.

Methyl Ethyl Ketone. The same data were obtained for methyl ethyl ketone-water, and samples were

Figure 2. Vapor Composition of Acetone-Water System at Several Pressures

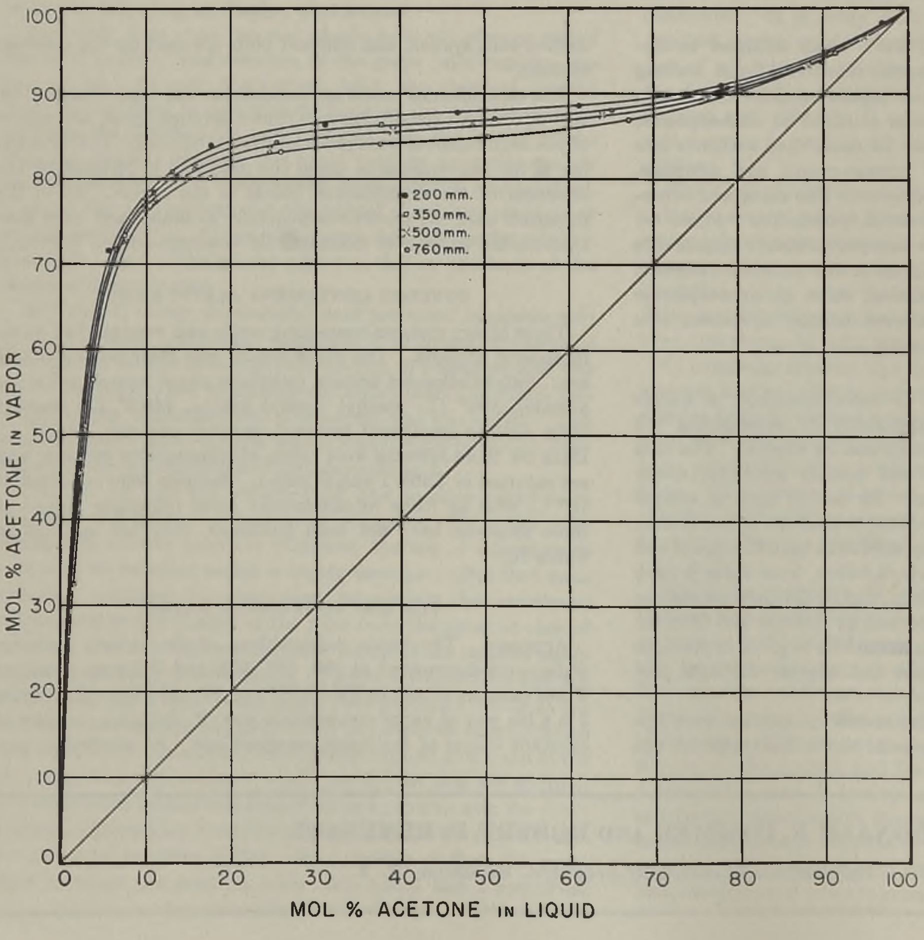

Table II. Refractive Indices for Solutions of Acetic Acid at 18.0° C.

Mole % HAc	Butyl Cellosolve Acetate	Methyl n-Amyl Ketone	Methyl n-Amyl Acetate
0	1.4144	1.4118	1.4013
10	1.4129	1.4102	1.4007
20	1.4114	1.4084	1.3998
30	1.4095	1.4065	1.3981
40	1.4070	1.4044	1.3960
50	1.4040	1.4016	1.3937
60	1.4007	1.3979	1.3936
70	1.3965	1.3933	1.3880
80	1.3908	1.3880	1.3837
90	1.3830	1.3815	1.3785
100	1.3724	1.3724	1.3724

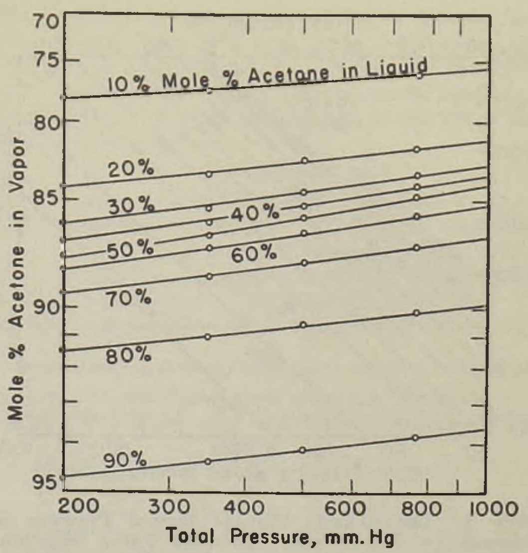

Figure 3. Logarithmic Plot of Mole Per Cent Acetone in Vapor vs. Total Pressure on System at Constant Mole Percentages of Acetone in Liquid

analyzed by specific gravity at 20° C. They are illustrated in Tables VII and VIII and Figure 6, and the log plot of y *vs.* P, the total pressure at constant x, is shown in Figure 7. Here again straight lines are obtained on the log plot. Figure 8 shows the comparison of these data at atmospheric pressure with that of other investigators (*8*) in a plot of $(y\text{-}x)$ *vs.* x.

The dashed line that cuts the y *vs.* x plot on the right in Figure 6 represents the limiting solubility of water in methyl ethyl ketone; that on the left represents the limiting solubility of methyl ethyl ketone in water from the data of the International Critical Tables (*4*). The horizontal portions of the vapor composition lines between these dotted lines represent the portion of the system of constant y with variable total x since there are in this range two phases in the liquid and variable amounts of these two phases; the composition of each is constant and is represented by the intersection with the respective dotted line. A single point on the horizontal portion thus fixes this entire range at the horizontal level of the composition of vapors, the boiling temperature (which was determined), and the corresponding mutual solubilities at this temperature, which are known. Data were not taken at superatmospheric pressure; but the horizontal straight portions would drop lower, less methyl ethyl ketone in the steam distillation or minimum constant-boiling mixture (c.b.m.), and would be shorter and shorter with increasing pressure. The dotted lines would continue and finally join to form a smooth loop, the lowest point of which would correspond to the highest temperature or critical point on the curve of temperature *vs.* mutual solubilities (International Critical Tables) which is roughly an inverted U. At that upper temperature limit (143°) of two phases in the still pot, the horizontal straight section would disappear, there would still be a c.b.m.,

Table III. Vapor Composition Data for Acetone-Water at Various Pressures (Experimental Data)

760 Mm. Hg			500 Mm. Hg		
x	y	t° C.	x	y	t° C.
0	0	100	0	0	88.7
1.5	32.5	89.6	2.8	50.7	71.4
3.6	56.4	79.4	6.1	73.3	62.3
7.4	73.4	68.3	7.5	72.6	59.6
17.5	80.0	63.7	11.0	77.1	56.8
25.9	83.1	61.1	14.9	78.7	55.0
37.7	84.0	60.5	15.7	81.4	52.7
50.5	84.9	59.9	24.6	83.5	51.3
67.1	86.8	59.0	39.2	85.7	49.4
80.4	90.2	58.1	48.6	86.5	48.6
89.9	93.8	57.4	64.0	87.4	47.9
			76.5	89.3	46.5
			88.2	93.3	45.7
			94.8	96.5	45.1

350 Mm. Hg			200 Mm. Hg		
x	y	t° C.	x	y	t° C.
0	0	...	0	0	66.4
2.1	47.1	66.6	3.4	60.1	48.1
6.5	71.6	53.0	5.5	71.5	41.5
11.2	76.5	48.5	15.4	79.2	33.2
10.8	78.4	47.4	17.7	83.9	30.7
13.6	80.1	45.8	31.1	86.2	27.6
13.0	80.8	46.2	46.8	87.6	25.9
25.4	84.1	41.9	61.2	88.5	24.8
37.9	86.3	40.1	78.0	90.9	23.8
51.2	87.0	39.4	90.3	94.7	22.8
65.1	88.0	37.9	96.8	98.2	22.3
78.8	90.6	37.1	100	100	21.8
91.5	94.7	36.2			

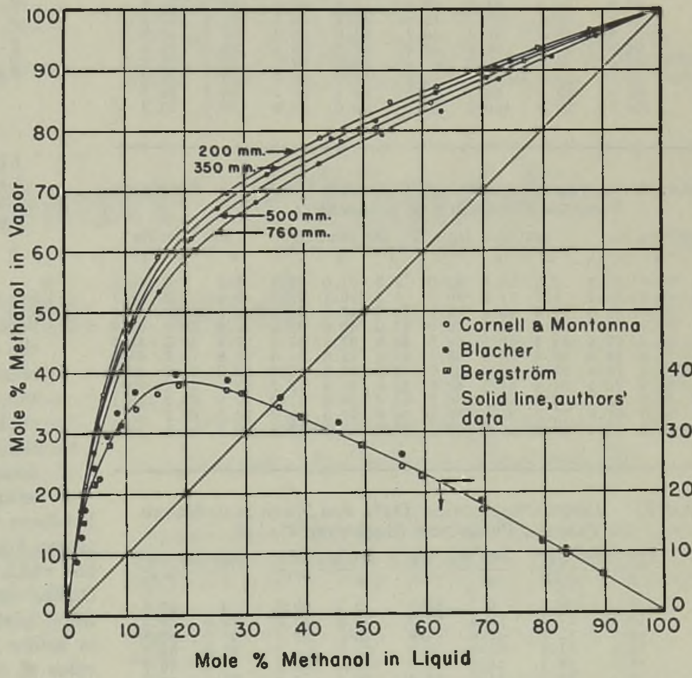

Figure 4. Vapor Composition of Methanol-Water Systems at Several Pressures in Upper Group of Lines

Lower loop is a plot of $(y\text{-}x)$ *vs.* x; the solid line indicates the present data and the points indicate the data of previous investigators.

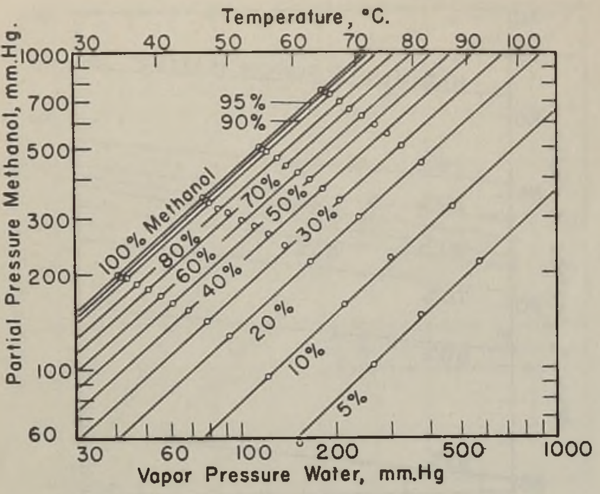

Figure 5. Logarithmic Plot of Partial Pressure of Methanol in Vapor over Methanol-Water Solutions *vs.* Vapor Pressure of Water at Same Temperature

Lines are for constant values of methanol in the liquid.

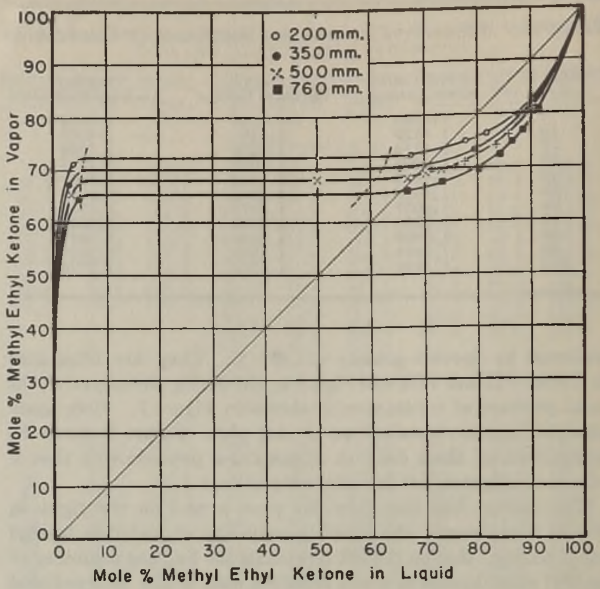

Figure 6. Vapor Compositions of Methyl Ethyl Ketone-Water Solutions at Indicated Pressures

Dotted lines represent limits of mutual solubility at respective temperatures of c.b.m. for indicated pressures and are terminals of straight sections of horizontal lines.

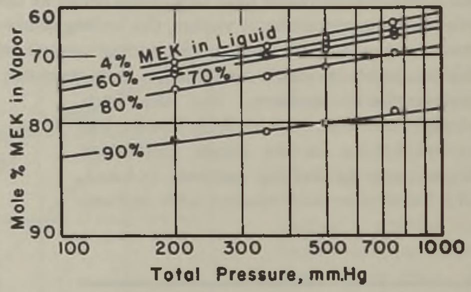

Figure 7. Logarithmic Plot of Mole Per Cent Methyl Ethyl Ketone in Vapor *vs.* Total Pressure at Constant Mole Percentages of Methyl Ethyl Ketone in Liquid

TABLE IV. VAPOR COMPOSITION DATA FOR ACETONE-WATER AT VARIOUS PRESSURES (SMOOTHED DATA)

	760 Mm. Hg		500 Mm. Hg		350 Mm. Hg		200 Mm. Hg	
x	y	t° C.	y	t° C.	y	t° C.	y	t° C.
0	0	100	0	88.7	0	79.6	0	66.5
1	34.0	92.5	32.5	79.0	29.5	73.4	22.7	57.5
3	50.0	82.1	53.0	70.5	57.0	63.3	48.5	49.0
6	67.5	73.0	69.4	63.3	70.4	55.2	71.8	43.0
10	76.0	67.8	76.6	57.5	77.3	49.2	78.2	36.5
20	81.7	62.4	82.6	52.2	83.4	43.3	84.3	30.1
30	83.5	60.5	84.6	50.5	85.4	41.0	86.3	27.6
40	84.2	60.1	85.4	49.4	86.2	39.8	87.2	26.4
50	84.8	59.8	86.0	48.7	86.8	39.0	87.9	25.6
60	85.8	59.5	86.6	48.0	87.5	38.4	88.5	24.8
70	87.4	58.9	88.2	47.2	88.7	37.7	89.5	24.3
80	90.1	58.2	90.5	46.4	91.0	36.9	91.5	23.6
90	93.8	57.3	94.1	45.5	94.4	36.2	94.7	22.7
100	100.0	56.5	100.0	47.7	100.0	35.5	100.0	21.8

TABLE V. VAPOR COMPOSITION DATA FOR METHANOL-WATER AT VARIOUS PRESSURES (EXPERIMENTAL DATA)

760 Mm. Hg			500 Mm. Hg			350 Mm. Hg			200 Mm. Hg		
x	y	t° C.	x	y	t° C.	x	y	t° C.	x	y	t° C.
4.6	26.7	92.7	2.5	16.3	85.0	3.3	21.0	74.7	1.3	9.5	64.8
9.4	40.2	88.1	5.5	31.0	80.2	5.1	30.1	72.6	2.5	17.0	63.1
15.7	53.3	84.0	11.4	48.4	75.4	10.6	47.8	67.6	6.4	36.3	59.2
21.7	60.2	80.8	21.2	62.2	70.0	17.9	60.0	63.2	15.6	59.0	52.0
32.1	68.0	77.4	32.5	69.6	66.5	25.6	67.1	59.6	27.4	69.6	47.3
42.5	74.5	74.8	46.3	78.2	63.1	33.9	72.6	57.3	42.8	78.6	43.3
53.4	79.1	72.4	52.3	80.4	62.0	44.5	78.6	55.0	54.3	84.8	40.9
63.2	82.9	70.5	61.4	84.5	59.7	52.3	81.4	53.2	62.5	87.2	39.5
72.7	88.3	68.7	70.9	88.7	58.7	62.4	86.2	51.3	72.2	90.5	38.1
81.7	92.0	67.3	77.2	91.3	57.7	74.9	91.5	49.0	79.5	93.7	37.1
89.1	95.6	66.1	88.0	95.8	56.0	87.4	95.9	47.4	88.5	96.6	35.8

TABLE VI. VAPOR COMPOSITION DATA FOR METHANOL-WATER AT VARIOUS PRESSURES (SMOOTHED DATA)

	760 Mm. Hg		500 Mm. Hg		350 Mm. Hg		200 Mm. Hg	
	y	t° C.	y	t° C.	y	t° C.	y	t° C.
0	0	100.0	0	88.7	0	79.6	0	66.5
5	28.4	92.3	29.5	81.2	29.5	72.9	29.0	60.5
10	42.7	87.7	45.0	76.6	45.7	68.1	47.0	55.6
20	58.6	81.6	60.8	70.4	62.3	62.3	63.0	50.1
30	66.3	78.1	68.5	67.2	70.9	58.4	71.3	46.7
40	72.4	75.5	74.5	64.6	76.4	55.8	77.1	44.1
50	77.6	73.3	79.5	62.4	80.9	53.7	82.1	41.9
60	82.8	71.1	84.0	60.6	85.2	51.7	86.2	40.1
70	87.7	69.1	88.2	58.9	89.5	49.8	89.8	38.5
80	92.0	67.4	92.6	57.3	93.3	48.3	93.5	37.0
90	96.0	65.9	96.6	55.9	97.2	47.1	97.0	35.6
100	100.0	64.5	00 0	54.7	100.0	46.4	100.0	34.3

but it would be the more normal shape of that of miscible liquids, although there would still be two liquid phases in the condensate. Of particular interest in considering the relation and definition of the terms c.b.m., azeotropic mixture, and steam distillation is the fact that in this system the horizontal straight lines (which define the steam distillation) and what is often called a heterogeneous azeotrope do not cross the 45° line. This crossing really defines a c.b.m. or an azeotropic mixture—i.e., one which boils unchanged). It follows that, for this special system, the azeotrope or c.b.m. is always homogeneous and hence falls to the right of the dashed line which represents the limit of solubility of water in ketone. On the other hand, the steam distillation or heterogeneous azeotropic mixture falls to the left of the limit of solubility of water in ketone and also to the left of the x-y line, so that the value of over-all y will always be different from that of the over-all x. Furthermore, it follows that, since the c.b.m. or point of crossing of the 45° line is the lowest boiling point, it must be slightly lower than that of the steam distillation. This difference in boiling temperatures or change in vapor composition (i.e., the elevation above the horizontal line of the point of crossing the 45° line) is, however, extremely slight. The peculiarities of this system are due to, or illustrated by, the fact that the right-hand solubility line, as indicated on the right-hand dashed line of the x-y plot falls to the left of the 45° diagonal.

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Appreciation is expressed to Salvatore J. Silvis, Sidney Seff, and Murray H. Edson for the determination of experimental data reported; and to Carbide and Carbon Chemicals Corporation for supplying many of the solvents used. The suggestions made by H. C. Carlson in the organization of the manuscript were most helpful.

Table VII. Vapor Composition Data for Methyl Ethyl Ketone–Water Systems at Indicated Pressures (Experimental Data)

760 Mm. Hg			500 Mm. Hg			350 Mm. Hg			200 Mm. Hg		
x	y	t° C.	x	y	t° C.	x	y	t° C.	x	y	t° C.
100	100	79.6	100	100	66.3	100	100	56.0	100	100	41.5
91.3	80.8	75.6	90.6	80.8	63.5	91.9	83.8	54.3	90.3	82.5	40.6
88.4	76.9	74.8	86.0	76.3	62.7	79.6	73.2	52.8	81.3	76.3	40.0
86.4	74.8	74.3	83.7	74.1	62.5	67.1	70.1	52.7	77.7	75.0	39.9
84.2	72.4	74.0	77.8	71.2	62.2	65.3	69.8	52.7	67.4	72.6	39.8
80.0	69.7	73.6	73.1	69.7	62.0	[a]	70.0	52.7	[a]	72.2	39.9
73.1	67.6	73.4	70.4	69.1	62.0	2.9	67.3	57.0	3.8	70.9	41.3
66.9	65.8	73.3	66.9	68.1	62.0	0	0		0	0	66.4
[a]	65.4	73.3	[a]	68.0	62.0						
4.8	64.4	73.9	3.4	65.2	64.8						
0	0	100	0	0	88.6						

[a] Two phases in liquid.

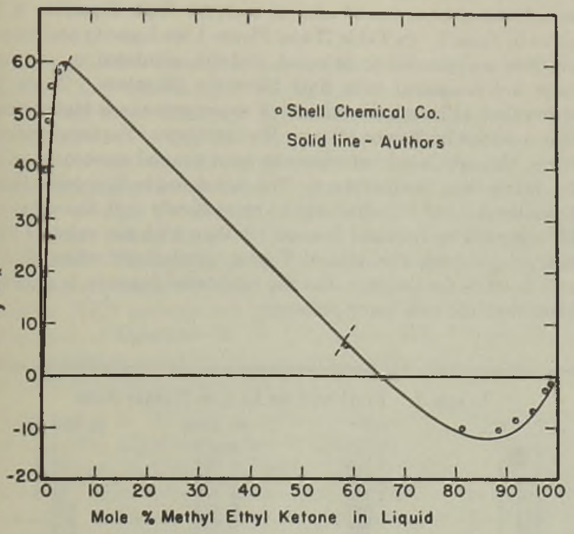

Figure 8. Difference of Vapor and Liquid Compositions (y-x) vs. Liquid Compositions (x) for Methyl Ketone–Water

Solid line represents experimental data; dots represent data of Shell Chemical Company.

Table VIII. Vapor Composition Data for Methyl Ethyl Ketone–Water Systems at Various Pressures (Smoothed Data)

	760 Mm. Hg		500 Mm. Hg		350 Mm. Hg		200 Mm. Hg	
x	y	t° C.	y	t° C.	y	t° C.	y	t° C.
0	0	100.0	0	86.6	0	79.5	0	66.3
3	61.1	77.0	64.0	66.7	67.2	56.6	69.5	42.8
5	64.5	73.4	67.7	62.3	69.6	53.0	62.1	40.1
10	65.1	73.2	68.0	62.0	70.0	52.3	72.0	39.9
20	65.1	73.2	68.0	62.0	70.0	52.3	72.0	39.9
30	65.1	73.2	68.0	62.0	70.0	52.3	72.0	39.9
40	65.1	73.2	68.0	62.0	70.0	52.3	72.0	39.9
50	65.1	73.2	68.0	62.0	70.0	52.3	72.0	39.9
60	65.2	73.2	68.0	62.0	70.0	52.3	72.0	39.9
70	66.2	73.3	68.8	62.1	70.4	52.4	72.7	40.1
80	69.5	73.6	72.1	62.2	73.3	52.9	75.5	40.0
90	78.4	75.2	80.4	63.3	81.1	53.9	82.0	40.4
100	100.0	79.5	100.0	66.3	100.0	56.0	100.0	41.4

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Vapor Pressure of Liquid Nitric Acid

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The vapor pressure of liquid (100%) nitric acid was calculated from thermodynamic data on the assumption that the fugacity and vapor pressure are equal. The calculated values agreed well with experimental data recently reported in the literature. The free energy equation for the vaporization of liquid nitric acid was found to be:

$$\Delta F^0 = 14{,}744 + 22.07T\ln T - 13.38 \times 10^{-3}T^2 - 166.26T$$

The boiling point of liquid nitric acid calculated from this equation is 84° C. Equations for the heat capacity of liquid and gaseous nitric acid were developed.

FORSYTHE and Giauque (*2*) recently published extensive thermodynamic data for nitric acid. They reported the heat capacities of liquid (100%) nitric acid and the heat contents of gaseous nitric acid; they calculated the free energy of formation of gaseous nitric acid at 298.1° K. on the basis of the free energy of formation of liquid nitric acid and the vapor pressure data of Wilson and Miles (*6*), which on extrapolation gave 62.9 mm. of mercury as the vapor pressure at 25° C. Forsythe and Giauque suggested but did not make the calculation of the fugacity of nitric acid from the data they presented.

The wartime demand for concentrated nitric acid has added practical significance to the theoretical interest in the vapor pressure of this acid. If the assumption is made that the fugacity of nitric acid is equal to the vapor pressure, the calculated fugacities can be compared directly with measured vapor pressures.

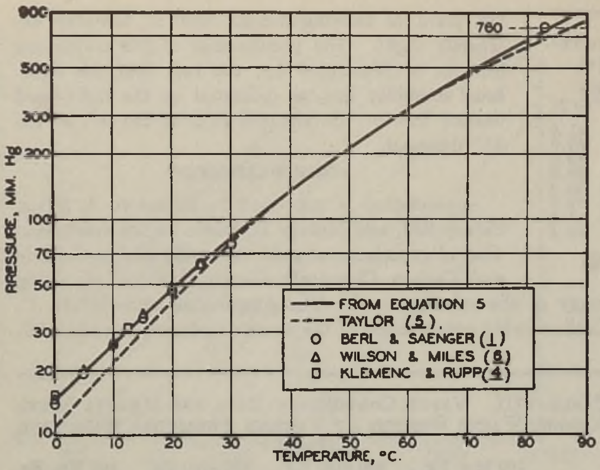

Figure 1. Vapor Pressure of Liquid Nitric Acid

The published data on vapor pressures of nitric acid and its aqueous solutions were compiled by Taylor (*5*) in 1925, and these data appear in the International Critical Tables (*3*). Taylor (*5*) reported that the data for solutions containing more than 70% nitric acid and for 100% (liquid) nitric acid were rather limited and inconsistent. Since 1925 a few data on the vapor pressure of liquid nitric acid have appeared; Wilson and Miles (*6*) made accurate measurements between 0° and 20° C., Klemenc and Rupp (*4*) made a few measurements in their study of the system HNO_3–NO_2, and Berl and Saenger (*1*) reported the boiling point of nitric acid as 83° C. at 760 mm. of mercury pressure.

The present paper gives heat capacity equations for liquid and gaseous nitric acid, an equation for the free energy of vaporization of nitric acid, and vapor pressure values calculated from the free energy equation on the assumption that the fugacity and vapor pressure are equal. The calculations are based chiefly on the data of Forsythe and Giauque (*2*).

The heat capacity equation for liquid nitric acid was derived from the measured heat capacities (*2*). The equation for gaseous nitric acid was derived from calculated heat contents (*2*); differentiation of the resultant heat content equation yielded the heat capacity equation. The values calculated from the derived equations agreed with the values reported by Forsythe and Giauque (*2*) within about 0.1%. The heat capacities of liquid and gaseous nitric acid may be expressed by the following equations over the indicated temperature ranges:

$$232° \text{ to } 305° \text{ K.: } C_p(\text{HNO}_3\text{, liquid}) = 28.64 - 8.0 \times 10^{-3}T \quad (1)$$

$$275° \text{ to } 500° \text{ K.: } C_p(\text{HNO}_3\text{, gas}) = 6.57 + 18.75 \times 10^{-3}T \quad (2)$$

Integration of the heat capacity equation for liquid nitric acid yielded the heat content equation:

$$(H^0 - H^0_0)/T = 28.64 - 0.004T \ (\text{HNO}_3\text{, liquid}) \quad (3)$$

At 298.1° K. the value of $(H^0 - H^0_0)/T$ is 27.45. The value of $(H^0 - H^0_0)/T$ at 298.1° K. for gaseous nitric acid is 9.37 (*2*, Table XVII). The heat of vaporization at 298.1° K., taken as the difference between the heats of formation of liquid and gaseous nitric acid (*2*), is 9355 calories per mole. Then, by the relation,

$$\frac{\Delta H^0_0}{T} = \frac{\Delta H^0}{T} - \frac{\Delta(H^0 - H^0_0)}{T} \quad (4)$$

ΔH^0_0 = 14,744 calories per mole of nitric acid vaporized at 298.1° K. The free energy of vaporization at 298.1° K. is 1476 calories per mole (*2*). By combination of the heat capacity equations for liquid and gaseous nitric acid, the calculated value for ΔH^0_0, and the free energy of vaporization of nitric acid at 298.1° K., the following equation for the free energy of vaporization was derived:

$$\text{HNO}_3 \text{ (liquid)} = \text{HNO}_3 \text{ (gas)} \quad (5)$$

$$\Delta F^0 = 14{,}744 + 22.07T \ln T - 13.38 \times 10^{-3}T^2 - 166.26T$$

This equation is valid only at temperatures within the range of overlap between Equations 1 and 2 (275° to 305° K.) but can be extrapolated to cover the temperature range 273.1° to 373.1° K. without the introduction of significant error. At pressures near 1 atmosphere the fugacity of nitric acid probably would be a few per cent smaller than the measured vapor pressure. The fugacity, as calculated in terms of mm. of mercury from Equation 5, is given in Table I. In Table II and Figure 1 the fugacity and vapor pressure are assumed to be equal, and the calculated vapor pressures are compared with data from the literature. Table II shows that, although the calculated vapor pressure is higher than that reported by Taylor (*5*) near the extremes of the temperature range, the calculated values are in good general agreement with the values from the literature. The calculated boiling point from Equation 5 is 84° C., which agrees more closely with the value of 83° reported by Berl and Saenger (*1*) than with the value of 87° interpolated from the data of Taylor, particularly when allowance is made for the fact that the calculated fugacity is slightly lower than the true vapor pressure.

Table I. Fugacity of Liquid Nitric Acid

T, ° K.	ΔF^0	K, Atm.	f, Mm. Hg
273.1	2,153	0.019	14.4
283.1	1,879	0.035	26.6
293.1	1,609	0.063	47.9
303.1	1,345	0.107	81.3
313.1	1,085	0.175	133
323.1	830	0.274	208
333.1	579	0.417	317
343.1	332	0.615	467
353.1	89	0.882	670
363.1	−151	1.233	937
373.1	−388	1.687	1282

Table II. Comparison between Calculated and Experimental Vapor Pressures of Liquid Nitric Acid

	Vapor Pressure, Mm. Hg				
T, ° C.	Calcd.[a]	Berl & Saenger (*1*)	Wilson & Miles (*6*)	Klemenc & Rupp (*4*)	Taylor (*5*)
0	14.4	14.0	14.7	14.9	11
5	19.7[b]	19.6	20.1	...	15
10	26.6	26.5	27.1	31.5[c]	22
15	35.7[b]	35.5	36.2	...	30
20	47.9	47.3	48.0	...	42
25	62.5[b]	61.0	62.9	62.1	57
30	81.3	77.4	..	...	77
40	133	...	..	...	133
50	208	...	..	...	215
60	317	...	..	...	320
70	467	...	..	...	460
80	670	...	..	...	625
90	937	...	..	...	820
100	1282	...	..	...	...
83	730[b]	760	..	...	668[b]
84	760[b]	...	..	...	700[b]
87	855[b]	...	..	...	760[b]

[a] Fugacity and vapor pressure assumed to be equal.
[b] From Figure 1.
[c] Temperature, 12.5° C.

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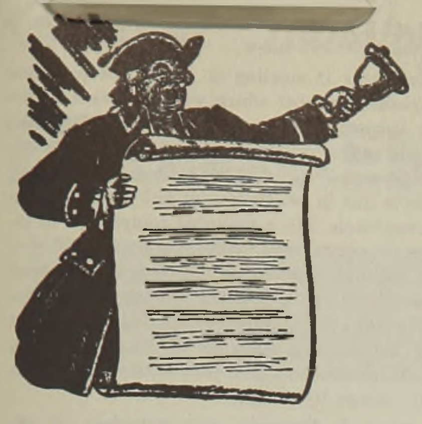

FEBRUARY'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ **February 1.** Houston, Texas, plant of Goodyear Synthetic Rubber Corp. turns out 100-millionth pound of synthetic rubber in slightly more than one year according to Superintendent C. W. Smith.∼∼Bakelite Corp. announces introduction of cold-setting phenolic resorcinol resin glue for wood bonding which provides maximum water resistance for exterior plywood applications.∼∼Paul B. Dunbar, Food and Drug Commissioner, announces drug manufacturers have withdrawn objections to plan of FDA for legislation requiring all penicillin to be certified as to purity and potency before entering interstate channels after present WPB controls are terminated[1].∼∼R. E. Wilson, new chairman of Standard Oil Co. of Indiana, tells Chicago chemists petroleum industry has become a larger volume producer of synthetic organic chemicals than the chemical industry[1].

¶ **February 2.** Gustav Egloff[2], president, American Institute of Chemists, announces award of institute's gold medal to John W. Thomas, chairman, Firestone Tire & Rubber.∼∼Department of Justice asks Supreme Court to clarify decision in glass container industry antitrust case involving seven concerns, among them Hartford-Empire, Corning Glass, Owens-Illinois, and Hazel Atlas.∼∼Foreign Economic Administrator Leo Crowley reveals that American shipments of petroleum products to Soviet Union under Lend-Lease up to Dec. 1, 1944, totaled 1,265,000 tons and 638,000 tons of chemicals.∼∼Department of Justice announces settlement of eight suits against Alien Property Custodian for recovery of 5903 shares of General Dyestuff Corp. stock. Alien Property Custodian obtains undisputed ownership of stock at $118 per share, book value being $540[3].

¶ **February 3.** Valentine Boucas, Brazilian head of organization handling Brazilian-American war materials agreement, predicts 40,000-ton rubber crop in 1945, of which U. S. will receive 30,000 tons.∼∼WPB forbids sale of nonessential products containing lead after Feb. 28.∼∼Goodyear announces construction of $10,000,000 factory at Nashville, Tenn., for manufacture of military truck tires, and important expansion of facilities at Topeka, Kans., plant for raw materials storage facilities.∼∼Army Ordnance plants producing at rates more than 40% greater than designed capacity at Buckeye Ordnance Works, Ironton, Ohio, and Ohio River Ordnance Works, Henderson, Ky., Brig. Gen. Stewart E. Reimel, chief, N. Y. Ordnance District, says.

¶ **February 5.** R. J. Dearborn, president, Texas Development Corp., and chairman, Committee on Patents, National Association of Manufacturers, says voluntary exchange of technical information should be continued after war to promote technological progress and jobs.∼∼Cooper-Bessemer Corp. develops Diesel engine which can operate with one fuel and then another, and will cut fuel consumption 20 to 25% when gas is used.∼∼WPB approves construction of $1,500,000 chemical plant at Natrium, W. Va., by Goodyear for manufacture of rubberlike plastics.∼∼U. S. Circuit Court of Appeals officially dockets Government appeal from district court ruling that Army seizure of Montgomery Ward properties was illegal.∼∼Forty companies manufacturing vitamins announce organization of Vitamin Research Institute of U. S., with Theodore Klumpp, president of Winthrop Chemical, as chairman of board of governors.

¶ **February 6.** National Foreign Trade Council, in resolution to members of Congress, outlines stand on cartel-like international business agreements and makes specific recommendations looking toward legalization of cartels.∼∼WPB reduces by another 5% use of new fiber shipping containers for nonmilitary purposes and tightens restrictions on their use in general.∼∼Lack of manpower cuts operations of three aluminum plants.

¶ **February 7.** WPB puts gum rosin, wood rosin, and nitrocellulose plastics under control of M-340 governing miscellaneous chemicals[4].∼∼Horace E. Riley, chairman, North Jersey Section, ACS, announces that Edwin R. Gilliland, former assistant rubber director, is first recipient of Leo Hendrick Baekeland Award.∼∼Brazil and Peru require special import licenses for certain goods, among them glass, nonmetallic minerals, minerals in general, and iron alloys.∼∼Attorney General Francis Biddle tells meeting of Kiwanis Clubs in New York that U.S. can defeat cartels if Americans refuse to participate in them.

¶ **February 8.** WPB orders four aluminum plants to increase ingot output by 10,000,000 pounds a month as soon as labor is available.

¶ **February 9.** WPB says, beginning with March allocations, the use of phthalic alkyd resins will be restricted to interior can and interior closure coatings for food, medical, and chemical purposes[5].∼∼WPB places yellow iron oxide pigments under allocation control of Schedule 90 of M-300 as of March 1[4].

¶ **February 12.** President Roosevelt tells Congress he will soon submit for congressional consideration a series of proposals covering control of cartels and orderly marketing of world surpluses of certain commodities; an international oil agreement; establishment of Food and Agriculture Organization of the United Nations; broadening and strengthening of Trade Agreements Act of 1934.∼∼Ministry of Information says lack of vital chemicals is contributing to France's inability to restore her industries.∼∼Du Pont offers 35 postgraduate fellowships at 29 universities for academic year 1945–46[3].∼∼Goodyear announces development of lightweight waterproof packaging and fabricating material Vitafilm, a derivative of polyvinyl chloride.∼∼Senator James E. Murray announces series of hearings to develop method for Government to dispose of investments in aluminum and magnesium plants, and assure entrance of many new concerns into the field.∼∼WPB decides to turn over penicillin distribution to regular pharmaceutical and chemical distribution channels March 15.∼∼War Food Administration reduces quotas of malt

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[1] *Chem. Eng. News*, 23, 352 (Feb. 25, 1945).

[2] *Ibid.*, 263 (Feb. 10, 1945).

[3] *Ibid.*, 353 (Feb. 25, 1945).

[4] *Ibid.*, 360 (Feb. 25, 1945).

to U. S. brewing industry to make more malted grain available for industrial alcohol and synthetic rubber.

¶ February 13. Monsanto Chemical announces it will not only manufacture launching propellent chemical for robot bombs, but will also be responsible for production of rocket motors.

¶ February 14. Petroleum Administration for War announces curbs on use of propane gas for civilian use.∼∼W. W. Cowgill, U. S. Rubber, predicts synthetic rubber production will be a $200,000,000 a year postwar industry in Southern California, and that national output will be in excess of $1,000,000,000 annually. ∼∼Wisconsin Alumni Research Foundation files reply in District Federal Court denying all accusations in government suit charging monopoly, price fixing, and other violations in marketing of patented vitamin D products.∼∼WPB Rubber Bureau announces extensive program to curtail consumption of carbon black by 10,000 pounds a month.∼∼Frederick J. Cullen, executive vice president, announces establishment of Office of Pharmacal Information by Proprietary Assoc. of America with headquarters in N. Y. and Washington.∼∼WPB places ethyl ether under control of Schedule 91 of Order M-300, general chemicals allocation order.∼∼Monsanto starts full-scale production at Duck River government-owned plant, which Monsanto operates for Chemical Warfare Service at Monsanto, Tenn.∼∼WPB further tightens supply of chemicals commonly used in production of semivitreous dinnerware for household use.

¶ February 15. Lederle Laboratories announce development by Raymond L. Libby, Cyanamid Research Laboratories, of method to make penicillin pills.∼∼John L. Collyer, president, announces that B. F. Goodrich Co. will construct research laboratory in Brecksville, Ohio.∼∼Col. Joaquin E. Zanetti, CWS, professor of chemistry and director of chemical laboratories, Columbia University, receives Legion of Merit award from War Department.∼∼Chester M. Alter, acting dean of Graduate School and professor of chemistry, Boston University, says U. S. faces grave shortage of trained scientists in postwar period. ∼∼Butadiene plant at Kobuta, Pa., produced at slightly better than 160% of rated capacity in January, Dan M. Rugg, vice president, Koppers Co., announces.∼∼Leonard H. Cretcher, assistant director of Mellon Institute, receives Pittsburgh Award for outstanding service to chemistry from Pittsburgh Section, ACS.∼∼Secretary of Interior Ickes reports that more helium will be available for nonmilitary purposes.

¶ February 16. Zinc will soon be put under allocation control, WPB announces.∼∼House Committee on Postwar Military Policy and Planning, headed by Representative Woodrum, holds hearings on proposed bill to establish a Research Board of National Security to continue the function of the Office of Scientific and Research Development on a permanent peacetime basis.

¶ February 17. War Mobilization and Reconversion Director Byrnes authorizes 15 government procurement agencies to make requests for deferment of men under 30 in key jobs in war factories.∼∼Secretary Ickes in annual report renews recommendation that Department of the Interior should encompass natural U. S. power resources in its role as steward for federally owned land and developments.∼∼Federal Judge Philip Forman fines 6 individuals and 18 companies a total of $240,000 on charges of conspiracy to fix prices since 1934 on stainless steel finished products.

¶ February 18. President Roosevelt authorizes seizure of American Enka Plant Corp., Asheville, N. C., producers of rayon cord and strike-bound since February 8.

¶ February 19. Department of Commerce report prepared in cooperation with WPB's Forest Products Bureau, says production of paper and paperboard in U. S. in first quarter of 1945 probably will be less than the established WPB program determination. ∼∼E. F. Riesing, chief automotive engineer, Firestone Industrial Products Co., demonstrates at meeting of ASTM metropolitan section, a type of synthetic rubber which will not freeze or become brittle under substratosphere conditions.∼∼OPA high officials ask Congress to extend price control powers until December 31, 1946.∼∼Representatives of WPB's Chemicals Bureau say that a sharp rise is due in production of anhydrous hydrofluoric acid.∼∼Pennsylvania Salt announces completion of installation of facilities for commercial manufacture of DDT.∼∼ WPB discloses that laminated wood for 11,000 keels has been produced in two years.∼∼General Electric announces development of new plastic for Navy that withstands fire and its resultant toxic effects during battle.∼∼Employees of American Enka Corp. filed back by the hundreds to their jobs in the rayon plant as an aftermath of its seizure by Army.

¶ February 20. James J. Newman, vice president, B. F. Goodrich, says synthetic rubber now constitutes 85% of the over-all volume of rubber America is using.∼∼Watson Davis, director, Science Clubs of America, says 260 high school students are honorable mention winners in Fourth Science Talent Search in competition for $11,000 in Westinghouse Science Scholarships. ∼∼WPB says use of carbon black in Grade A camelback for recapping passenger car and small truck tires will be indefinitely postponed on account of carbon black shortages.∼∼E. W. Tinker, executive secretary, American Paper and Pulp Assoc., in annual report advocates a 9-point stabilization program to meet increasing pulp and paper demands.

¶ February 21. Survey by petroleum reserves committee of American Petroleum Institute shows net gain in Nation's proved crude oil reserves of 389,079,000 bbl.

¶ February 22. Commercial Solvents in annual report discloses that its penicillin plant at Terre Haute, Ind., is producing 50% more penicillin than maximum for which plant was designed. ∼∼American Cyanamid announces purchase of 800 acres of land along Ohio River near St. Marys, W. Va., for Calco Chemical Division.∼∼Chairman Connolly of Senate Foreign Relations Committee says industry is generally favorable to proposed new Anglo-American petroleum agreement, which removes compulsory powers of projected international commissions.∼∼WPB estimates January liquor "holiday" will bring beverage alcohol output to about 59,000,000 proof gallons.

¶ February 23. PAW announces that 5 additional 100-octane plants will be constructed and that proposals for several more are being studied.∼∼WPB's Rubber Bureau says that DPC has authorized funds for 4 new heavy tire production projects.

¶ February 24. Selective Service headquarters announces that men aged 30 through 33 will have to meet more rigid specifications to be eligible for occupational deferment.∼∼Secretary Ickes announces selection of site near Rifle, Colo., for a $1,500,000 oil plant to test processes for getting oil from shale.∼∼President signs George bill divorcing federal lending agencies from Department of Commerce.

¶ February 25. Lucas P. Kyrides, research director of Monsanto's Organic Chemicals Division, winner of first Midwest Award of ACS St. Louis Section. Award will be made annually for "meritorious contribution to advancement of pure or applied chemistry or chemical education". Eligible for the honor are chemists residing in nine states in Midwest[5].

¶ February 26. WPB says it will protect only the "vital hard core" of essential workers under 30 in certifying men for occupational deferment from the draft.

¶ February 27. William Y. Elliott, WPB vice chairman, proposes postwar establishment of international bauxite allocation committee to plan for production and distribution of bauxite and aluminum.

¶ February 28. WPB says printing paper production will be cut April 1.

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[5] *Chem. Eng. News*, 23, 320 (Feb. 25, 1945).

Current Developments in
EQUIPMENT AND DESIGN

With present knowledge of heat transfer has come appreciation of the role of surface through which heat flows.

Discussed by Charles Owen Brown

One of the most important subjects to chemical engineers is heat transfer. To equipment manufacturers the design of surfaces through which heat flows has always been of interest because surface represents expense, and that design which could be most heavily loaded and simply constructed proved to be most profitable. Without claiming great accuracy for timing, we wish to recall some of the successful and profitable attempts to build, into equipment, designs for heat transfer perfection.

We cannot remember details of any equipment accurately previous to 1908, when the Dopp kettle was acknowledged to be an improvement for boiling operations. This kettle was cast in the usual hemispherical shape with a steam jacket generously braced to the kettle shell with stay-bolt-like pins, which were cast integral with jacket and kettle. The entire kettle was a one-piece casting. Since these stays were not through bolts like the usual stay bolts, leaks could not occur and the Dopps were known justly as "good kettles". It was also accepted without question that, since this stayed jacket permitted the use of steam at higher pressures than was possible in ordinary cast-iron kettles, the capacity for boiling, or the heat transfer rate, was higher. This was quite elementary; but if the fact that the one-piece stay bolts (because they were integral with the kettle wall) increased the heat transfer rate, this sales point was not illuminated with sufficient candle power to penetrate the writer's mind. Understanding came with experience; a film of solid phenol in a cold kettle always melted in round spots opposite each cast stay several seconds before the film as a whole melted. The transfer rate was greater at the surface opposite the integral stays.

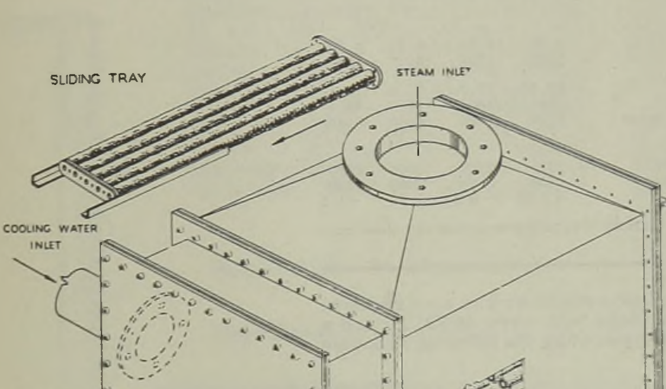

Figure 1. Dawes Condenser Unit Which Encloses 314 Lineal Feet of Special Extruded Surface Tubing; in Testing It Condenses 7200 Pounds of Steam at 266° F. per Hour.

Several years after the appearance of Dopp kettles, an American firm introduced a clever piece of fabrication in the Frederking, now called Thermocoil, kettles. These kettles were made by enclosing a shaped steel pipe coil within the cast-iron or cast-steel walls and bottom of the kettle. The high transfer rates possible in this kettle depended primarily upon higher-pressure steam. The steel coils were safe for appreciably higher working pressures than the steel pipe alone. In some applications the maximum transfer rate could not be used without burning the stock because maximum heat flow in this kettle was based upon a high working temperature and large temperature differences rather than upon an extended surface like the stays in the Dopp. Advances in the theory of the film concept of heat transfer were applied to efficient designs by the equipment manufacturers. A large part of the development work was devoted to economical methods of attaching fins and other forms of extended surface rigidly in contact with tubes, for heaters, coolers, and vacuum steam condensers.

Foster Wheeler Corporation perfected small cast-iron rings with several circular fins on each ring. Good contact between rings and the steel tube was obtained by machining the inside of each ring to a close tolerance, heating, and then shrinking successive rings on the tube until it was completely covered. Griscom-Russell Company experimented with thin, punched disk washers which were then pressed on tubes in a regular spacing. Later this method was changed in favor of the well-known K Fin tubing, consisting of thin strips of metal bent edgewise in spirals on a tube which had been grooved to take the inner edge of the strip. Good contact was obtained by peening the edge of the groove to the strip. In place of spiral strips around the tube, this manufacturer of heat exchange equipment has attached long, straight fins to tubes parallel to the center axis, known as G Fins. This last construction has given excellent results in countercurrent heat exchangers, where water or steam flows in forced connection or turbulence inside of the fin tube, while gas to be cooled or heated flows outside the tube between the fins and an outer pipe, closely enclosing the finned tube. Excellent continuous contact has been made between the inner edge of each fin and the tube. Brown Fintubes are similar in appearance, but are made differently. Long thin strips of metal are bent into a trough-shaped U-section which is resistance-welded at the bottom to the tube, parallel to the axis; properly spaced, these strips complete the circle around the tube, each U-section adding two fins.

The designs briefly described above represent a great deal of study and tooling, much of which could have been avoided if it were possible to extrude carbon and alloy steel tubes with fins in place. Although this is impossible for carbon steels, the light metals and some copper alloys are extruded as fin tubes at a considerable cost saving for a high-quality article.

The application of extended surface tubes to commercial equipment is typically shown in the small vacuum steam condenser illustrated in Figure 1. A comparison of the heat transfer rates in this equipment with the older smooth-tube construction is interesting. The design shown was developed by B. P. Dawes with John L. Trebilcock for Contract Engineering, San Francisco. The most important feature of this new condenser is the type and arrangement of the tubes, and (*Continued on page 72*)

design features throughout which give compactness and high capacity. The total volume is about one third and the weight about two thirds of the usual smooth tube condenser of the same capacity; these features are advantageous in installation and, later, in cost of repairs and ease of maintenance. Steam (or any condensable vapor) enters the body of the condenser at the top, contacting the outside extended surface of the tubes. Water or condensate is pumped out through an opening at the side bottom, and air is withdrawn above on the side. The remarkably short tubes are mounted on tray-like frames which are quickly installed or withdrawn, and can be repaired or retubed on an ordinary workbench. Ample trays of tubes are mounted between two divided compartment plates, in a file cabinet arrangement. Water enters the upper compartment, passes through half the tubes, returns through the remaining tubes, into the second compartment, and out. Three flanges in the body of the condenser are required for assembly.

Tests have been made of a Dawes condenser measuring 2 × 3 feet and 3 feet long, equipped with 314 lineal feet of the special extended surface tubing arranged in twenty-six trays, of five tubes each. The test was run condensing steam with water at 77° F. The condenser vacuum ranged from 12.8 to 27.2 inches of mercury, and water velocities in the tube were varied from 5.52 to 7.28 feet per second. The results of these tests, summarized in Table I, show credible performance.

Table I. Performance Data and Results for Dawes Condenser

(130$^5/_8$ inch i.d. × 30 inch copper extruded tubes; water in at upper of two tube passes)

Duration, minutes	55	30	69	33
Test number	16	13	12	14
Exhaust steam inlet				
Pressure (referred to 30-in. Hg barometer)				
In. Hg vacuum	12.8	18.7	25.8	27.2
In. Hg abs.	17.2	11.3	4.2	2.8
Superheat,[a] ° F.	83	105	128	128
Condensate				
Rate (by weighing), lb./hr.	7120	5723	3356	2350
Temperature, ° F.	183.5	163.3	123.5	110
Cooling water				
Rates				
Velocity, ft./sec.	6.45	6.34	6.30	6.36
By weighing, lb./min.	3205	3235	3220	3250
Temperature, ° F.				
In	77.9	77.7	72.6	71.1
Out	116.1	108.9	91.3	84.1
Head loss through tubes, ft. water	3.04	3.25	3.36	3.36
Heat balance				
Loss by steam, 1000 B.t.u./hr.	7310	6010	3640	2570
Gain by water, 1000 B.t.u./hr.	7350	6050	3640	2520
Difference, %	+0.55	−0.83	0.00	−1.6

[a] Based on calorimeter measurement of supply steam enthalpy (heat content).

A comparison test of the Dawes condenser with a conventional smooth-tube condenser was made with water at 73° F., and a vacuum of 26 inches of mercury in which the following data were taken:

	Dawes Condenser Test Data	Smooth-Tube Condenser Calcd. Data
Vacuum, inches Hg	26	26
Steam, lb./hr.	3620	3900
Cooling water, gal./min.	447	440
Inlet temperature, ° F.	73	73
Outlet temperature, ° F.	90.4	89.77
Cooling-water velocity, ft./sec.	7.28	7.0
Cooling-water temp. rise, ° F.	17.4	16.77
B.t.u. removed per hr.	3,900,000	3,900,000
Condenser surface, sq. ft.	64	123
Heat transfer factor U, B.t.u./sq ft./hr./° F. ltd.	1365	730

This test reveals a small, compact, and efficient condenser, suitable for service with small steam turbines used on process equipment drives. The over-all U value for the Dawes condenser is not strictly accurate because the exact surface area, said to be 64 square feet, may be debatable. One can appreciate the magnitude of the transfer coefficient from the inside smooth area of 314 lineal feet of tubing, about $^5/_8$ inch in diameter.

Current Developments in

INSTRUMENTATION

Distillation of vitamins, drying of penicillin, manufacture of magnesium, etc., all involve operations at low pressures. Instruments for measuring these pressures are discussed here.

Discussed by Ralph H. Munch

OPERATING under vacuum is one of the most useful methods of lowering the temperature required for distilling, subliming, or drying a substance. A short time ago plant chemists considered that they were carrying out an extremely difficult operation if they used these processes below 10 mm. In those days there was little or no plant-scale equipment designed to produce, to operate at, or to measure pressures below that value. The McLeod, the Pirani, and the ionization gages were the playthings of physicists. Now, these and other types of gages for measuring low pressures are available commercially, in some cases even in the form of recorders or controllers.

For pressures down to 10 mm., closed-end manometers such as those made by The Meriam Instrument Company, of Cleveland, are perhaps the most satisfactory pressure-measuring devices. They are simple and accurate, and do not require calibration against a standard. To keep them readable, they should be protected by traps chosen to exclude dirt and corrosive fumes. A little care in choosing and installing proper traps will appreciably lengthen the useful life of manometers, and will result in more accurate readings and worth-while savings in replacement costs.

A vacuum gage useful over the range from about 25 mm. down to 1 mm. is the float-type manometer, sometimes known as the DuBrovin gage. Although this kind of manometer is old, few chemists and chemical engineers are acquainted with it: F. E. E. Germann and K. A. Gagos discussed its operating principles in INDUSTRIAL AND ENGINEERING CHEMISTRY, ANALYTICAL EDITION, 15, 285 (1943). Briefly, this type of manometer, one form of which is shown in Figure 1, consists of a tube with one end closed, inverted in a somewhat larger tube which is a little over twice its own length and is half full of mercury. The float is centered in the larger tube by two sets of three projections, one at the top and one at the bottom. This type of gage is prepared for use by evacuating it while it is in a horizontal position and bringing it to a vertical position while evacuated. This is the zero pressure position of the float. When the pressure in the space above the float is increased, the float sinks lower into the mercury until the downward pressure on the float is counterbalanced by the upward force of buoyancy on its submerged portion. The float of a gage like that shown in Figure 1 moves 7 mm. for a 1-mm. change in pressure if it is made of 13-mm. Pyrex tubing with a 0.4-mm. wall. This type of manometer has been found useful in plant operations involving pressure down to 1 mm. It can be easily made by a moderately skillful glass blower, gives a continuous indication of the total pressure in the system, including that due to condensable vapors, and can be easily read to 0.1 mm. A commercial variety of this gage, known as the DuBrovin gage, can be obtained from the W. M. Welch Scientific Co., Chicago.

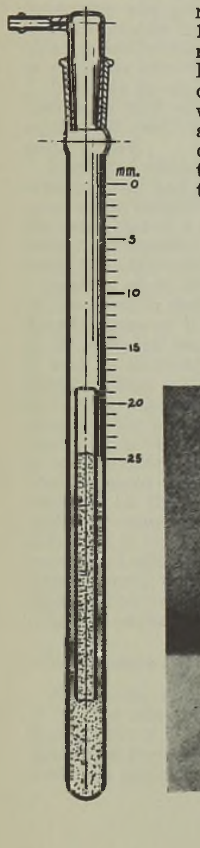

Figure 1 (*Left*). Float-Type Manometer

Figure 2 (*Below*). Pirani Gage

The McLeod gage serves to measure pressures from about 5 mm. down to a fraction of a micron. Although it is generally considered a primary standard for the measurement of low pressures in the laboratory, it suffers from disadvantages which make it inconvenient for plant use. One of these is that the readings are not continuous; to obtain readings, the mercury must be raised to compress the gas in the bulb into the capillary, then lowered to allow pressure equilibrium between gage and system to be established again. Another is that condensable vapors and gases which deviate from the gas law are not correctly measured. However, when its failings are known and taken into account, it is often quite useful. A convenient compact form of McLeod gage is made and sold commercially by F. J. Stokes Machine Co., Philadelphia. This gage is obtainable in three ranges, 0 to 5000, 0 to 700, and 0 to 70 microns.

The Pirani type vacuum gage measures gas pressures by determining the thermal loss from a heated filament. Since this thermal loss is a function of the pressure of the gas around the filament, it can be used to indicate gas pressure. The useful pressure range of this instrument is from 3 mm. to a fraction of a micron. Calibration of the Pirani gage depends on the gas. Since the thermal losses are measured electrically, this type can give a continuous indication or even record and control the pressure in a system.

A Pirani gage made by Distillation Products, Inc., of Rochester, N. Y., is shown in Figure 2. The type PG-1A gage employs a carefully matched pair of Pirani tubes attached to the control box by a 9-foot cable. The portable control box contains two meters, one to indicate bridge voltage, and the other calibrated in pressure units in two ranges, 0 to 20 microns and 0 to 0.75 mm. Additional pairs of matched tubes can be supplied so that the pressure can be read at more than one point on the vacuum system. The range of the instrument can be varied to include pressures as high as 3 to 4 mm., provided adjustments are made in the type of tube used and the scale range.

The Televac type MR vacuum recorder, distributed by Precision Scientific Co., of Chicago, is a recording Pirani gage with a range of 0 to 500 microns. The record is produced by a Leeds & Northrup Micromax strip chart recorder with a special pressure scale. The makers state that the instrument is extremely stable under all conditions due, primarily, to specially treated filaments in the Pirani tubes.

(*Continued on page 78*)

Instrumentation

Pressures in the range from 10^{-3} to 10^{-4} mm. can best be measured with an ionization gage. The ionization gage consists of a vacuum tube with filament, grid, and plate, provided with a tubulation for attaching it to the vacuum system. In operation, electrons passing from the filament to the grid, which serves as the anode, ionize a certain fraction of the residual gas molecules. These positive ions are collected by the plate which is maintained at a slight negative potential. For a given electron current and gas, the positive ion current is proportional to the gas pressure in the gage. Pressure measurements with this gage are therefore made by measuring electrical currents.

The Distillation Products type HG-200 gage is a typical commercial ionization manometer. It incorporates a power supply for the ionization tube, a control circuit to keep the electron current constant, and an amplifier for measuring the ion current. It covers the complete range 10^{-3} to 10^{-9} mm.

The model S Televac distributed by Precision Scientific Co. is a pressure recorder using both a Pirani and an ionization gage. From atmospheric pressure down to 10^{-3} mm. the instrument records pressure as indicated by the Pirani tube. At that pressure the recorder trips a relay that makes it possible to turn on the ionization gage which serves to record pressures from 4×10^{-4} down to 10^{-6} mm. It is impossible to turn on the ionization gage until the pressure is low enough for its use; if by some accident the pressure exceeds the safe limit for the ion gage while it is in use, the recorder turns it off immediately. This feature prevents filament burn out and greatly lengthens the life of the ion gage.

The Moore Products Co., Philadelphia, has just announced a new development in liquid-level controllers. Their engineering department has devised methods which make it possible to produce the standard Moore packless, flexible shaft type, liquid-level controller with all parts which come in contact with the liquid made of Hastelloy B. This construction imparts a high degree of corrosion resistance.

Figure 3 shows a group of these controllers. The motion of the float is transmitted to the pilot mechanism through a packless flexible shaft, which eliminates the use of packing glands. The flexible portion of this shaft is similar to a Bourdon tube in cross section, as the photograph shows. Manufacture of a device such as this from Hastelloy B is quite a manufacturing achievement. These controllers are also available in neoprene-covered and in rubber-covered construction, among other types.

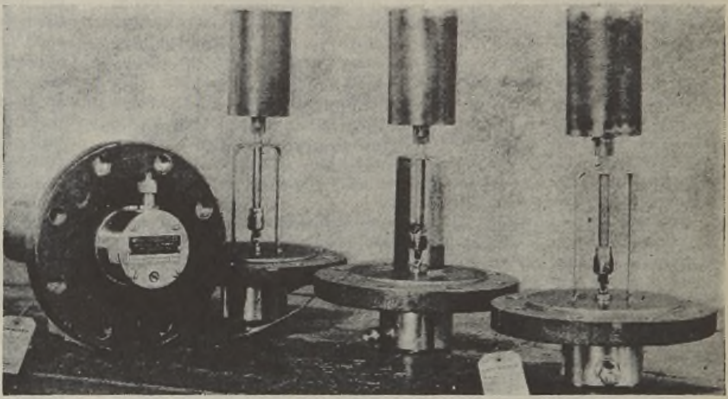

Figure 3. Liquid-Level Controller

Current Developments in
PLANT MANAGEMENT

Successful reconversion from war to peacetime production will depend on the ability of industry to lay out new production procedures efficiently and put them into operation quickly.

Discussed by Walter von Pechmann

In the near future the already overburdened production executive will have to devote part of his time to the layout of new production procedures. Our present discussion is intended to give him assistance in carrying out this task by calling to his attention some of the important points he will have to consider.

It is common practice to separate the layout of a procedure from its execution and to assign each phase to different personnel. This has the advantage that responsibilities are clearly defined. However, it does not take into consideration the necessity of convincing production that the proposed method is feasible, and considerable time may have to be spent adjusting minor inaccuracies in the original layout. Failure to give sufficient consideration to these phases has caused many a well-planned procedure to fail. Furthermore, in order to ensure proper operation, new procedures must be closely followed up until they have become routine. This work should always be considered as part of the installation of a procedure.

The writer has made it a practice to approach new procedures in the following three phases: (1) layout; (2) obtaining cooperation from production and revising original layout to fit production requirements; and (3) supervision until the procedure has become routine.

Layout

Most people are inclined to consider improper layout the most common cause of the failure of procedures. The writer had adhered to this theory for many years. However, a study made to determine why production procedures had not worked out, revealed that only in a few instances was improper layout to blame. The reasons for failure due to improper layout are given herewith in sequence according to the frequency with which they occur: 1. Inability to explain or write up procedures properly. 2. Interference with existing procedures. 3. Improper estimates of equipment performance. 4. Improper estimates of personnel performance.

Employes assigned to the layout of procedures are usually well qualified and do not ordinarily commit these errors. However, where basically new procedures have to be laid out or where the originator of a procedure is not entirely familiar with the details of production, it is essential to consult the people who will have to do the work. In these instances the writer usually calls a meeting which is attended by foremen and key workers. He develops, with their cooperation, work flow charts on a blackboard. Because it is not always possible to draw immediately, in chronological sequence, all the phases involved in the procedure, it may be necessary first to write on the board the important phases as they come to mind and later to arrange them in proper numerical sequence. It is good practice to combine several phases of the same nature under one heading in order to indicate more clearly the major steps. It is also possible to make a draft of written instructions by writing on a piece of paper the suggestions received and by identifying the papers according to the numbers on the blackboard which correspond with the phase under discussion. Later the work flow chart can be drawn and displayed in work rooms. The numbers on the flow chart will correspond with the finished numbered instructions which will also be issued; employees then will be able quickly to gain knowledge of how to perform a job in the event they should have forgotten verbal instructions.

Assurance of Cooperation

Regardless of how carefully a procedure has been designed, difficulties must be expected when it is first put into operation. Recognition of this fact is important because it will not discourage the person responsible for the installation if everything does not work out according to plan. Furthermore, it will prevent him from discrediting the layout immediately after encountering the first objections from production. It would be unwise, however, to consider these difficulties as a natural adjunct of a new procedure and expect them to be self-adjusting. Changes must be made quickly and efficiently by both the person who designs the original layout and the person responsible for the installation of the procedure. Emphasis is placed on the cooperation of both parties. The writer recommends the abolishment of the frequent practice of handing a layout to someone down the line to "take care of the details". Procedures handled in this manner are often doomed before they are put into operation and, at best, will represent a poor facsimile of the originator's plans.

Resistance encountered from production when installing a new procedure can frequently be disposed of by informing employees in detail of the reasons for the procedure. The assumption that the very nature of a system will indicate to employees the reasons for the establishment is erroneous. Anyone familiar with psychology will admit that these employees will connect a change of working conditions with something affecting themselves unless they are otherwise informed. Here are some remarks which may sound familiar to production men: "This system was installed to make us work harder." "The new setup is intended to give management an opportunity to evaluate us." "This procedure will restrain the foreman from bossing us around as he pleases."

It is not infrequent that the foreman in the shop raises objection to the installation of a new procedure. It would be wrong to conclude hastily that this constitutes lack of good will. It is considered good practice to listen to him and to have him suggest other means to bring about desired results. On the other hand, if he objects on general principles to the installation of a procedure decided upon by management or cannot furnish any other objections than to state that the procedure "is not practical", it must be considered a waste of time to indulge in lengthy discussions.

Time Factor

Objections dealing with the time factor have to be dealt with most commonly. It is often believed that sufficient time will not be available for compliance with the requirements laid out in the new procedure. This is due to the fact that the foreman overestimates the effort necessary to bring about a job performance under normal operating conditions; he lacks the knowledge to judge how much a time cycle can be reduced after the employees have become used to the new procedure. The statement that "things will get better, as time goes on" is not sufficiently convincing to satisfy a foreman. A method which usually brings good results is to chart graphically the time necessary to perform an operation from the beginning of a new procedure to the time it has become routine, and to show the foreman the graph. This will convince him quickly that his present objections may not be justified a week later.

Sufficient time must be given for the adjustment of personnel. This obvious fact is mentioned because production executives occasionally forget that a reported increase in labor hours was due to the installation of a new procedure and therefore asked the foreman for an explanation. This tends to make the foreman hesitant in willingly accepting new procedures.

Occasionally the time factor is overstated by the foreman in order to avoid additional work or responsibility. The writer views with suspicion the statements that additional recordings cannot be made because of lack of time. If records are properly designed, entries can be made with little effort and loss of production time. However, no one should expect the foreman to lay out forms; this is the job assigned to the person responsible for the original layout.

The fact that the procedure has been

(Continued on page 84)

Plant Management

laid out completely does not necessitate its entire installation at one time. Contrary to common belief, procedures are most successfully put into operation by retaining initially all the phases of the old procedure which do not interfere with the new priniple to be applied. This reduces the number of factors to be changed at one time and gives employees an opportunity for gradua adjustment. Use of this method is recommended where the full cooperation of production employees cannot be obtained at the start of a procedure, or in the event the new procedure contains a great number of phases unfamiliar to workers.

It is advisable to keep in mind that the original layout can be changed extensively to fit production requirements without departing from the principle laid down. This applies especially to the change of names commonly used in production. The writer does not hesitate to incorporate in written instructions terms which are used in the shop although they might not be entirely correct from the chemist's point of view. Consideration should also be given the fact that the requirements of a new procedure may have to be adjusted to fit standards prevailing in the shop. If it should be found, for instance, that the original layout calls for the accumulation of time in quarter hours, but the time clocks record in tenths of hours, instructions should be changed accordingly. The theory that matters of this nature do not have to be adjusted because employees, for example, have no choice but to record their time in tenths of hours, is faulty; no consideration has been given the fact that workers sooner or later will point to this instance in an attempt to prove that instructions cannot be carried out.

Follow-up

In order to stress the importance of the follow-up, the writer once installed three procedures in different sections of a department and assigned one foreman to follow them up. The foreman was instructed to check procedure 1 daily for one week, every second day the following week, and once weekly from then on. Procedure 2 was checked once weekly, and procedure 3 remained unchecked. The number of violations were observed, recorded, and later charted. This was the finding:

PROCEDURE 1 was in force at the time the test was completed (3 months).

PROCEDURE 2. During the first weeks, violations increased from day to day, declined after the weekly check, only to increase again shortly thereafter. Total number of violations decreased from week to week. However, the procedure was not functioning properly after 3 months.

PROCEDURE 3. Violations increased quickly. After 3 weeks the procedure was practically nonexistent. After 3 months the majority of employees claimed the procedure was never installed.

This test may not be entirely conclusive; nevertheless it revealed several interesting facts: (1) New procedures will not function properly if no follow-up is made. (2) It is important that frequent checks are made at the beginning. (3) By properly selecting the intervals of supervision, the number of checks can be reduced. (4) For best results the time between each check should be increased gradually.

Occasionally one hears the remark that production executives cannot devote their valuable time to the follow-up of new production procedures. Executive supervision can be performed with little effort and in a very short time if the correct method is used. I refer to control by exceptions. This system is based on the belief that the executive is not interested in what is right; he wants to know what is wrong. Therefore, he establishes limitations which, when exceeded, will have to be reported to him. The report, however, indicates only the extent of the violation above or below the limits set. Applying this system to the follow-up of new procedures, production executives should have little difficulty in obtaining information regarding the status of newly installed procedures.

In conclusion, the writer would like to call attention to a simple but, nevertheless, effective means of promoting interest among workers for new procedures: use of sketches or photographs in place of symbols for all major steps on the flow chart. It is not uncommon to see a group of employees gathered in front of such a flow chart. Although it is the original intention to criticize the sketch or photograph, conversations usually end up in a discussion of the new procedure.

Last-Minute Flashes

FROM THE EDITOR'S DESK

ONE of the tightest situations in the entire material picture is in plastics. This is specially true of those based in part on formaldehyde. Little relief is expected in the near future. Methanol production has given way to ammonia because of the stepped-up munitions program.

★ In the strictly natural raw material field, linseed is one of the biggest headaches, or rather the lack of adequate supplies is the big headache to paint manufacturers.

★ The second, or January, "whisky holiday" produced some 52 million gallons of beverage spirits, but the distillers are not too happy since nearly half of this is in the form of bourbon and hence not ready for immediate use. The 25 million gallons of neutral spirits, of course, can be used to assist in stretching out existing supplies. In the August holiday no bourbon was made because corn was not available to the distillers.

★ Washington is a spot where almost any set of figures can be obtained to prove a point. Whereas the cutback after Germany is defeated was described three months ago as likely to be as heavy as 40%, the figure now being bandied about is 17%. Probably it will be somewhere between—possibly nearer 40%.

★ The 1944 production of rayon in the United States totaled 742 million pounds, made up of 571 million pounds of filament yarns and 171 million of staple fiber. Acetate production amounted to 23% of the total rayon output; cuprammonium, slightly over 1%; and viscose, about 72%. Aralac, nylon, Binyon, etc., the newer synthetics, accounted for about 4%. *Rayon Textile Monthly* points out that the term "rayon" has now had 20 years of wide acceptance. Time does march on, for it seems only a few years ago that this was a red-hot editorial subject.

★ Insecticide manufacturers and others have been advised that DDT will be released only for experimental and research purposes. Compounders of insecticides will have to get along with the old stand-by products and should place orders promptly.

★ Controls on penicillin for civilian use are likely to be lifted soon. Military supplies are being built up at an encouraging rate.

★ There is some doubt in Washington that the heavy demand for phthalic anhydride can be met unless a still more ambitious plant expansion program is adopted.

★ According to reports from abroad, Germany's monthly output of synthetic oil is 100,000 tons or less a month, as compared with 500,000 tons which used to flow from some eighty plants.

★ Considerable stress has been brought to bear in many and varied quarters on the desirability of the United States "Lend-Leasing" scientific and technological assistance hither and yon in the postwar era. Latest to belabor the point is Vice Chairman Batt of WPB who suggested to the Engineering Society of Cincinnati that "one way the United States can help Britain back to her feet after the war is by lending her technological help".

★ Old Man Winter took a toll of chemical production in the Niagara frontier area during the past two months. Failure to receive raw materials and shortages of tank cars hurt the record of this important chemical producing area.