# INDUSTRIAL AND ENGINEERING CHEMISTRY

# **Production on the Wing**!

Throughout the nation production is soaring. But it must move still faster. Wartime demands, in ever-increasing volume, are pouring in upon manufacturers.

Every day, chemists and production executives engaged in new fields of work are faced with new problems. Every day, their need for tonnage chemicals of exacting specifications is more urgent. To these men, Baker offers assistance. We, too, have enlarged our facilities and you can get tonnage chemicals of unusual purity from Baker.

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**Baker's Chemicals** 

FINE

In the nation's leading laboratories, Baker's Analyzed C.P. Chemicals and Acids continue to be used to determine the *qualities* and properties of countless products.

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J. T. Baker Chemical Co. Executive Offices and Plant: Phillipsburg, N. J. Branch Offices: New York, Philadelphia and Chicago.

INDUCTRIA



# DICALITE FOR



HEAT-SAVING INSULATION



CATALYTIC AND ABSORBENT PROCESSES, FILTRATION, ETC.



CAMOUFLAGE AND OTHER WAR FINISHES

 By far the greatest portion of Dicalite output is today being utilized by the process industries and others vitally important in "Production for Victory." For example:

DICALITE HIGH TEMPERATURE INSULATION is saving valuable coal, oil and gas in operation of boilers, furnaces, kilns and other heated equipment. In our warships on the high seas, in iron and steel plants, smelters, power plants and like industries working full speed on war production, time and fuel are being saved and efficiency increased by use of Dicalite insulated construction.

DICALITE CATALYST CARRIERS, ABSORBENTS: In many process plants, Dicalite materials are used as catalyst carriers, absorbents and fillers, to increase production, save needed time and help speed the war effort. Petroleum refining, manufacture of many chemicals, citric acid and explosives are examples in point. Likewise, DICALITE FILTERAIDS insure fast and efficient filtration in producing such wartime necessities as oils, chemicals, food products and varnish.

DICALITE EXTENDERS AND FLATTING AGENTS effectively produce required flatness in camouflage paints and similar war finishes, also giving other desired qualities and conserving essential pigments and resins. DICALITE MINERAL FILLERS also speed production and improve quality of paper, asphalt products, rubber, plastics, and others.

• A Dicalite Engineer will gladly be of service in problems involving insulation, absorbents, fillers, filtration and other applications where diatomaceous products may be employed.

### THE DICALITE 520 N. Michigan Ave., CHICAGO • 120 Wall St., NEW YORK • 756 So. Broadway, LOS ANGEL

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INDUSTRIAL AND ENGINEERING CHEMISTRY INDUSTRIAL EDITION

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# In these 4 ways J-M Filtration Engineers may be able to help you

Boost Output with Your Present Filtration Equipment!

By selecting the Filter Aid for your particular process which provides the desired clarity with the highest flow rate. (See chart).

4

2

By determining exactly the right amount of Filter Aid to be added to the liquid to be filtered.

By determining the proper length of the filter cycle and the proper application of the filter powder.

By recommending a change or adjustment in the conditions of pH, temperature, concentration, viscosity or some other factor which may affect your filtering capacity.

WITH the aid of J-M Filtration Engineers, many manufacturers—unable to get additional filtering equipment—have substantially increased their filter capacity, some by three and four times.

Naturally, we can't promise you, until we've examined your operations, whether or not we can do as well for you. But this we can say: If it is possible to speed up filtration processes, and still meet required clarity specifications, it's almost certain J-M Engineers can help you do it!

Although J-M produces 10 different grades of Celite Filter Aids, there is only *one* which is just right for your particular process. That is the one which gives you the clarity you need . . . with the *highest possible flow rate*.

J-M Filtration Engineers can help you select the Celite Filter Aid which meets these requirements. Get the benefits of this service now, by writing



Johns-Manville, 22 East 40th St., New York, N. Y.

**Relative rates** of flow of ten different Celite Filter Aids are shown here. The correct filter aid for any particular problem is the one which gives the required clarity with the highest flow rate.

CELITE is available for prompt shipment!

# **UM Johns-Manville**

Filter-Cel ... Celite No. 505 ... Standard Super-Cel ... Celite No. 512 ... Celite No. 536 ... Hyflo Super-Cel ... Celite No. 501 ... Celite No. 503 ... Celite No. 535 ... Celite No. 545

\*

GERE BAR Ains GIVE MAXIMUM FLOW RATES WITH REQUIRED CLARITY

ON EVERY FILTRATION SERVICE



▶ OUR YEAP OF WAR and events in the chemical world caused or vitally influenced by that fact are reviewed (page 5) to provide a basis for new progress in the stirring days ahead. These developments are already forming into the foundations of a materially altered world again at peace, for which we must prepare.

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► FOOD AND NUTRITION loom large in present thinking, and the techniques involved are undergoing a revolution under the urgency of war's demands. Various aspects of this subject are discussed in some detail in a symposium of seventeen papers in this issue.

▶ MEAT DEHYDRATED by new processes is very different from what we have known in the past. The new methods developed for solving the problems of concentrating and preserving meat today are described in some detail by Kraybill (page 46), who also points out some of the probable consequences of this important innovation.

▶ FRUITS AND VEGETABLES, normally containing large proportions of water in the fresh state, lend themselves readily to dehydration processes. Preservation of maximum nutritional values requires modification of traditional methods in important particulars, according to Cruess (page 53). Modern procedures are described.

► CANNING TECHNOLOGY is in the midst of revolutionary changes to meet the problems arising out of the critical shortage of tin. Cameron (page 38) describes the means now in various stages of development to meet this situation, both as to containers and modified processing.

▶ REPRIGERATION applied in various ways is an essential factor in the problem of food supply. Pennington (page 62) discusses the applications of cold for preserving food, and points out the values and limitations encountered under existing conditions.

▶ FREEZING as a method of preservation of food has achieved increasing success through the careful choice and preparation of the raw products, according to DeFelice (page 26). Production by quick-freezing plants has undergone rapid recent expansion.

▶ COLD STORAGE has long been an essential factor in conserving food supplies. Lythgoe (page 29) brings us up to date on the many aspects of this subject in an inclusive survey of its important phases and its applications to current pressing problems.

▶ FATS in many foods undergo oxidative changes resulting in rancidity. Control of these reactions and stabilization of fats can be accomplished by the use of antioxidants, either natural or added, according to Mitchell and Black (page 50).

► SENSITIVITY OF VITAMINS and other essential factors in foods to processing procedures require recognition of the losses of nutritional value incurred and modification of methods to minimize them. Howe (page 24) discusses these aspects of the problems of food processing.

▶ FEEDING ARMED FORCES widely dispersed throughout the world entails many problems vital to the effectiveness of our arms. Wodicka (page 12) reviews accomplishments in this field, limiting requirements, and problems yet to be solved. ▶ PACKAGING Foods to withstand the varied and severe conditions encountered in supplying troops in widely separated arenas of war requires the employment of special measures to ensure safe delivery. Melson (page 16) describes methods employed in the face of present critical shortages of certain packaging materials.

▶ PROTECTION OF FOODS against possible chemical warfare agents is essential to armies in the field. Katz (page 20) has examined various packaging materials and methods to determine their values in this respect, and gives details regarding them.

▶ PACKAGING TRENDS are being affected fundamentally by scarcity of materials and by requirements for overseas shipment of sensitive commodities, according to Warth (page 43). Various factors entering the choice of packages are given.

▶ ENRICHMENT OF FLOUR and bakery products by the addition of vitamins and essential minerals has become standard practice. Catheart (page 66) reviews progress under legally established requirements for flour and voluntary measures taken with respect to bread and baked products.

▶ PEAS and other green vegetables undergo changes of color during ordinary canning operations. Blair and Ayres (page 85) have investigated this and other related phenomena, and suggest modifications to preserve color, flavor, and nutritional values.

▶ JUICES OF FRUITS and vegetables have within a decade grown immensely in commercial importance as foods. Improved methods of preparation and preservation are the factors principally responsible for the amazing popularity of juices, according to Tressler, Pederson, and Beattie (page 96).

▶ PASTEURIZATION OF MILK, long a standard procedure, still presents problems. Ball (page 71) discusses short-time hightemperature pasteurization in some detail and presents a method of control of this process based on analogies with canned foods.

► SANITATION is the prime requisite in the food industry, and consequently efficient detergents are vital to its operations. Parker (page 100) suggests that combinations of organic acids, having inherent inhibiting effects on bacteria, with surface-active agents and corrosion inhibitors have superior detergency as compared with most alkaline products.

► CELLULOSE FIBER preparations have been examined by Barnes and Burton (page 120) using both a light microscope and an electron microscope.

▶ SURFACE-ACTIVE AGENTS commercially available in the United States are listed with important facts about each by Van Antwerpen (page 126).

► SURFACE-ACTIVE AGENTS can be synthesized on the basis of known characteristics of intramolecular groups to meet almost any requirement, according to Snell (page 107).

Dotkieleffer

# Dry, heat process or bond non-conducting materials uniformly and rapidly with Thermex!

THERMEX

High Frequency

Heating



Principle of High Frequency Electrostatic Heating.

How Thermex Operates.

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Advantages of Thermex.

Applications for Thermex

Power Flow Diagram of Thermex.



6

Thermex high fre-quency electrostatic equipment simply ap-plies the principle in-volved in generating heat by molecular friction. That is, heat may be generated within a ma-terial by subjecting it to an electro-static field. Thermex is the first practical, proved equipment for com-mercial uses. mercial uses.

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THE GIRDLER CORPORATION

To help you visualize the possible applications of high frequency electrostatic heating to your operations, we invite you to write for a new booklet fully describing Thermex and its many uses. Mail the convenient coupon now!

#### Rapid, uniform heating regardless of thickness!

• A few advantages of Thermex high frequency electrostatic heating equipment:

NEW

BOOKLET

fully describes

process and

applications

Uniform heating throughout. Speed of heating never before attained. Applies to all non-metallic materials. No redistribution of moisture. Less handling required. Reduces labor costs. Handles wide variety of jobs with high efficiency. Results may be reproduced with-out variation. No surface damage or danger of over-heating. Heating may be suspended immediately. No "hot plates" or steam required. Wide range of sizes for all requirements.

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- THE GIRDLER CORPORATION Thermex Division 219 E. Broadway, Louisville, Ky. Send us your free booklet on Thermex High Frequency Heating:

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# HOW TO MAKE CHAIN DRIVES RUN BETTER --- LAST LONGER

**1** Keep shafts exactly parallel, and wheels exactly in line. Misalignment causes uneven loading and unnecessary wear.

**2** Remove chain frequently and clean thoroughly in some solution to wash out harmful dirt and grit. Then immerse in oil.

**3** Protect chain and wheels from needless exposure to abrasive materials, dust and dampness. Use oil-tight casings with high-speed silent or roller chain drives.

**4** Inspect shaft bearings by removing grease from bearing ends to expose the actual bearing metal. Rebabbitt if needed.

**5** Flush ball or roller bearings periodically with fresh grease to drive out foreign matter and replenish the seals. In dusty atmosphere or dirty locations, use auxiliary dust seals.

**6** Check machinery supports for vibration and reinforce if necessary.





**7** Operate chain with a little more slack than normal for a flat belt. Tight drives wear chain and sprockets needlessly.

#### **8** WHAT TO DO FOR WORN CHAIN

Turning a chain over so that the opposite side contacts the sprockets is a quick and easy means of restoring the original backing dimensions on cast pintle chains. On roller chains of either cast or steel fabricated types, this same simple operation will bring practically new surfaces into play under the rollers. In designs where pins are locked against rotation, wear is confined to that side against which the next link is held under tension. Rotating these pins 180°, places articulation action upon a practically unused pin area and, as far as the pins are concerned, restores original pitch. Bushed type chains afford another opportunity for pitch correction by reversing the bushings or rotating them 180°, but this involves the dismantling and reassembly of heavy press fits and should be avoided except as a last resort.



Turn Pins Half-Way Around to Place Wear on Unused Surface



#### 9 WHAT TO DO FOR WORN SPROCKETS

Cast-tooth sprockets, particularly in the larger diameters, frequently can be reversed on the shaft to bring chain barrels, or rollers, into contact with unworn root-diameter surfaces, but worn root-diameters on all types may be built up by welding and grinding smooth to fit the chain. Should wear have deformed the teeth of cast-tooth wheels into a hook-shape, these hooks may be ground off, or the wheels reversed.



\* Second in the series of advertisements written in the interest of efficient war production.

TO DO A BIGGER WAR JOB WITH STAINLESS STEEL EQUIPMENT

Remember this about priorities for stainless steel processing equipment—if your equipment employs more metal than is absolutely necessary for the application, there may be a plane or tank less for our fighting men.

DESIGN TO SAVE STEEL

To conserve steel while assuring the highest degree of performance, design your equipment to use lighter gauges of stainless steel with *rein*forcing structures that assure necessary strength.

Our engineers have had extensive experience in applying the principle of reinforcement to stainless steel processing vessels. Through the knowledge we have gained in fifty years of specializing in the fabrication of alloy processing equipment we can make available to you proved methods for making lighter gauge stainless steel do the work of heavier gauges.

Consult with us for engineering suggestions that will give your equipment high operating efficiency while saving steel for that extra plane or tank for our armed forces.



To assure equipment soundly engineered -to guarantee greatest fabricating economies - S. Blickman, Inc. maintains a large staff of electrical, civil, chemical, and mechanical engineers who are specialists in the design of stainless steel equipment up to  $\lambda_0^{u}$  thick. Below, one of the drafting rooms at the Blickman plant.

"What to Look for When You Specify Stainless Steel for Your Processing Equipment." a valuable guide for engineers, will be sent on request to those who write us on their company stationery.



ALL ORDERS SUBJECT TO GOVERNMENT PRIORITY REGULATIONS





COAL is one of our most useful as well as most plentiful raw materials. Its high value as fuel eclipses other services coal renders, but these extend into many diverse fields, both through the products of carbonization and otherwise. Progress in these respects will be reviewed for us next month. Coal products find increasingly important applications in agriculture where they perform the greatest variety of tasks. Anthracite coal is proving efficient as a filtering medium, particularly for water supplies and like problems, about which details will be supplied. Production of coke is a timely topic in view of magnified metallurgical demands. Two aspects of this problem will be discussed: blending of southern coals to produce foundry coke and effects of slow oxidative changes on storage of coal upon its caking and coking properties. As new developments in organic compounds of high molecular weight increase needs for them, techniques have been improved for recovering substances of this kind from coal without the destruction of molecular aggregates characteristic of coking. Some of these newer methods and their products will be described for us next month.

Although coal has wide interest, research and the problems of management connected with it are virtually universal in their importance to us. The techniques of managing research to attain maximum benefits have been worked out superlatively well by some of our leading organizations, while others find problems of this kind more troublesome than the scientific ones of the laboratory. That lends particular interest to a group of three papers planned for February publication on as many aspects of this major problem of industry. We shall learn something of the place of research in industrial organizations, valuable material for both administrative and scientific departments. Accounting and the control of expenditures on research will be clarified by a review of successful methods. The question of how far industry should go in research in its own organization is partly answered by graduate fellowship system which provides a useful means of amplifying the research functions and facilities of industry.

Ionic exchange agents have progressed far as means of reducing concentrations of both anions and cations in solutions. We shall learn of a two-step process for lowering electrolyte concentrations.

New data on the traditional "strength" test for starches and the relation of the results to true viscosity will be given.

Our data on hydrocarbons is to be amplified next month by values on n-butane systems—one, the hydrocarbon with hydrogen, and the other, with gaseous hydrochloric acid as the second component.

Grading of soft sugars by color of transmitted light has been previously described. Our next offering utilizes photoelectric measurements of reflectance for a similar purpose, using a specially modified instrument which may have other value.

Rubber solutions and gels are examined in the light of newly derived expressions for thermodynamic properties of solutions of long-chain molecules with interesting conclusions bearing on the basic problem of polymers.

New light is shed on the functions and behavior of additives (accelerators and pigments) in rubber by x-ray studies to be reported in February.

## UN <u>PPPPPPP</u>

SULFUR AND SULFURIC ACID ARE **VITAL BY-PRODUCTS OF GAS MIXTURES** PURIFIED BY THE GIRBOTOL PROCESS

• If the removal of hydrogen sulfide from the gaseous or liquid mixtures in any of your processes is desirable, you should consider the commercial possibilities of recovering this by-product, H<sub>2</sub>S, for sulfur and sulfuric acid production.

Or if you use sulfur in any of your processes, hydrogen sulfide usually can be recovered much more cheaply than sulfur can be purchased. Hydrogen sulfide can readily be burned to sulfur dioxide which is converted to sulfuric acid. The conversion of H<sub>2</sub>S to free sulfur has been carried on commercially abroad for several years, and recently has been operated successfully in this country.

The Girbotol Process removes and recovers acidic constituents from gaseous or liquid mixtures and does the job more completely and at less cost than any other method known today.

SULPHURIC

H2SO4

The Girbotol Process offers several interesting and valuable advantages in addition to scrubbing and recovering  $H_2S$  and  $CO_2$ . It offers simultaneous dehydration, is equally effective with high and low H<sub>2</sub>S or CO<sub>2</sub> contents. Plants are available in six standard sizes, as well as in large, individually engineered units.

Write today for further informa-tion about the Girbotol Process.

#### Processes for

Other Girbotol use

Protection of catalysi against injury by His in several processes.

Removal of CO. before ammonia synthesis in the manufacture of munitions.

Production of inert

Recovery of CO. from combustion gases such as coal broduction of liquid CO. production of liquid CO.

atmospheres.

Production, Purification, Separation, Reforming or Dehydration of

> HYDROGEN SULFIDE CARBON MONOXIDE BLUE WATER GAS ORGANIC SULFUR CARBON DIOXIDE HYDROCARBONS HYDROGEN NITROGEN OXYGEN

and various mixtures.







Frick Steam Engine of the Fifties



Steam-driven Refrigerating Machine, 1883



Enclosed Ammonia Compressor, Introduced 1915



Now Serves over 200 Industries and Businesses In 1850, to be exact, a millwright named George Frick built his first steam engine, and began the work which now means so much to the Victory Program.

By 1860 the Frick shops at Waynesboro were producing hundreds of engines. (General Lee's men, during the retreat from Gettysburg, took the belting from the plant, for use as shoe leather.)

By the time of the Spanish-American War, Frick refrigerating machines, introduced in 1882, were used in large numbers for packing meats, making ice, and storing essential foods.

By 1917 the importance of refrigeration was more fully appreciated. Thousands of Frick machines, in powder plants, hospitals, camps, ships, and supply bases, helped America win.

In the present conflict our refrigerating, ice-making and air conditioning systems play a still more vital part. Glenn Martin airplanes; Lycoming engines; Pratt and Whitney gauges; Hercules powder; important government buildings; scores of Army camps, Navy ships, arsenals, food factories, and civilian activities find Frick Equipment an invaluable aid.





HE first ad striking l our attention this month is that of Swenson Evaporator Com-They pany. talk about their favorite subject is, which strangely enough, filters and filtration

equipment. Through their years of experience Swenson says, they have learned not only what to do, but what not to do. That, we hold, is important, because in chemical engineering, as in the Good Book, sins of commission as well as omission are held against you. There is also a sketch showing the Swenson Top-Feed filter which, if my memory serves me right, was only an idea a few years ago, and it took a lot of first class engineering to lick the problem and make the idea work.

If the need for a special pump is keeping you awake nights as "Specs", blueprints, and operating requirements go chasing themselves through your weary dome, perhaps Gast can help you out. Cast your troubles on Gast, as it were. They have a long background in making special pumps, both vacuum and pressure type, for various applications. The rotary design of gas equipment makes for smooth and nonpulsating flow, and they also have an automatic take-up which compensates for wear. The Crane Company touches a vital subject this month. "Let's get in the scrap", they say, "but not make it." Their particular interest, of course, is in the conservation and reclaiming of valves which have served their purpose, but which could be used for other applications if correct salvage methods were used. They offer their "Piping Pointers", Bulletin No. 5, to help you get the idea of saving valves across to new men, and old.

Fumes resulting from acid operations can often be a nuisance to the neighborhood surrounding the plant. The Claude B. Schneible Company brings out some important "dope" when they talk about their multiwash collectors. They show an installation put in one mill which safely scrubs 125,000 cubic feet per minute of acid-containing air. Schneible builds the towers of any material best suited to resist the particular dust or fumes encountered, and towers are made in capacities up to 30,000 cubic feet per minute. Have you a fuming problem?

Industrial instruments have put Solu-Bridge in many war plants where it is standing watch over possible contamination of heat exchange systems. Solu-Bridge is an electronic device which measures the conductivity of water, and if acid should leak into the system, the cell and controls correct the trouble.

Important tips on how to make chain drives run better and last longer by Link Belt will be required reading for the operating engineers in our plants. They have nine important suggestions for conservation.

Taylor Instruments have two important developments which you should know about if you are planning to control temperatures within the limits of  $-100^{\circ}$  and  $+1000^{\circ}$  F. The first is a tubing containing a special alloy wire, which has a coefficient of expansion so related to the tubing and the mercury that any variations in temperature along the way are counteracted on the spot. The second development, quite important to our chemical engineers, is a special thermospeed separable well which eliminates response lags and therefore makes for quicker recording.

COL OID

# How Tube-Turn welding fittings speed-up



## piping installation for war production!



EASIER, FASTER, SAFER WELDING Tube-Turn fittings require only easy circumfer-ential butt welds-which insure faster, better, safer welding by both veteran and novice operators.



NO THREADS TO CUT Welding removes the inefficiencies of threaded joints, plus the labor and time applied to thread-Tube-Turn fittings come ready to install. ing.



FEWER FLANGED JOINTS SPEED ERECTION Welding fittings supplant the need for many of the flanged joints necessary in screwed piping, which materially reduces over-all erection time.

TRADE MARK



ALIGNING TIME GREATLY REDUCED Tube-Turn fittings simplify lining-up operations -because their uniform wall thickness and true circularity permit quick alignment with pipe.



NO TORCH CUTTING OR FABRICATION Since all Tube-Turn fittings are installed with easy-to-make butt welds, they eliminate time-consuming, complicated cutting and fabricating.



FEWER HANGERS OR SUPPORTS NEEDED As welded piping weighs less and stands vibra-tion better than flanged systems, the fewer hang-ers needed save installation time on these items.



WHOLE SECTIONS CAN BE PRE-ASSEMBL As Tube-Turn fittings and welded joints sta strain and save weight, piping sections can welded on the ground to save time, then erect



FASTER AND EASIER TO INSULA Tube-Turn fittings are insulated as readily as pipe, for the welds form one continuous tube. Eli inating many flanged joints shortens covering tir

. . And you get stronger, leakpro systems that virtually elimina piping maintenance or failure that can slow down or paraly; vital war industry! TUBE TURNS 11

INCORPORATED Branch Offices: New York, Chi-cago, Philadelphia, Pittsburgh, Cleveland, Dayton, Washiagton, D. C., Tulsa, Houston, Los Angeles. Distributors everywhere.

TUBE-TURN Welding Fittings

INDUSTRIAL AND ENGINEERING CHEMISTRY

Vol. 35, No. 1



# SABOTAGE ... from the air

Sharp...jagged...destructive! Not bombs. Merely little specks of dust ... but far from harmless, as highpowered microscopes would show.

It is easy to imagine what damage these hard, jagged particles can do to precision finished bearing surfaces in equipment ranging from delicate instruments to heavy machines. When a highly finished part must be scrapped because of dust-damage, much more is lost than just a piece of metal. Many hours of expensive, painstaking labor are completely wasted.

One of the best defenses against dust-sabotage is air conditioning... the specially designed kind of air conditioning which, through efficient air filtering and accurate control of temperature and humidity, is making possible precision tolerances never before attainable.

General Electric has taken an outstanding part in the development of this new air conditioning. Already, the war has taught us how to make equipment more compact, more flexible, and far more efficient. Required "climates" are faithfully reproduced. When the war is over, air conditioning...better, cheaper, more universally used...will do much to make the world of the future happier and more useful for everyone. Then, as now—General Electric will be a leading source of all kinds of air conditioning.

Air Conditioning and Commercial Refrigeration Department, Division 431, General Electric Co., Bloomfield, N. J.

Air Conditioning by GENERAL & ELECTRIC







DRYING - Vitamins

EVAPORATION Research

# To Help You PLAN PLAN TODAY TODAY

N striving to meet the seemingly impossible production requirements and changed processes imposed by the war, many American manufacturers are keenly aware of the inadeguacy of their present equipment. The major problem, in most cases, is one of equipment conversion . . . to meet today's needs with yesterday's equipment, and still plan for tomorrow.

To solve such problems successfully often requires more than a conference of plant executives. It's a job for men who have served the whole processing industry; and who are, therefore, abreast; or even ahead of the times in creative design. This is a job requiring combined technical advice with adequate research facilities.

To help you with such problems, we invite you to write to the BUFLOVAK Department . . . Submit your problems to them — they can offer many valuable suggestions.

If they haven't the answer, they will get it for you. The combined facilities of the BUFLOVAK Engineering Department, Research and Testing Plants is the source from which more than 4000 processing problems involving drying, evaporation, extraction, impregnation, solvent recovery, crystallization, etc., have been successfully handled during the past 40 years.

Send us your problem in detail and we will submit a complete, unbiased report or suggestion prepared by our Technical Staff.

Buffalo Foundry & Machine Co.

1549 Fillmore Ave.

Buffalo, N. Y.

DESIGNERS AND BUILDERS OF Autoclaves Vacuum Rotary Dryers Atmospheric Drum Dryers Pan Dryers Evaporators Chemical Plant Equipment Vacuum Drum Dryers Flakers Vacuum Shelf Dryers Rotary Dryers Impregnators Solvent Recovery Equipment

in the Processing Industries is a long time . . . It is forty years of growth through service for BUFLOVAK!

**40 YEARS** 

# never had a chance!

/alve

HIS iron gate valve was closed with scale or other matter lodged between the seat ring and wedge faces. If the leakage resulting from this condition had been heeded, and the valve properly inspected, the damage could have been prevented. Instead, unchecked leakage over a long period developed wire drawing effects. When belated inspection was made, the parts were so badly eroded replacement was essential.

his

Such neglect is a frequent cause of gate valve failure. Guard against this destruction by blowing out pipe lines freely as often as necessary, and by immediate inspection whenever leakage occurs.

In today's emergency, valves must be kept in efficient operation, not only to avoid production slow-downs, but to conserve valve metals, all of which are in urgent demand for actual weapons of

war. New valves can be obtained only for certain uses which are vital to the war effort. Many valves in present use must be kept in service until the war is won.

The well-known "ounce of prevention" is worth a pound of cure in valve maintenance. Inspect them frequently, systematically. Repair or replace worn parts before resultant deterioration begins. Be sure new maintenance men are thoroughly instructed. Select new valves for approved construction with extra

care, and see that they are installed properly by experienced workmen.

TO DESTRUCTION DOOMED

when tell-tale leakage went unheeded · · ·

Check up on your program of valve conservation and see that it is adequate to the present emergency. Jenkins Engineers will give you complete cooperation.



Army-Navy "E" Penant, awarded to Jenking Bros. for high achieve-ment in the production of war equipment.



Jenkins Bros., 80 White Street, New York, N. Y.; Bridgeport, Conn.; Atlanta, Ga.; Boston, Mass.; Phila-delphis, Pa.; Chicago, Ill.; Jenkins Bros., Limited, Montreal; London, England.





# "Eyes Right" Has Never Meant So Much To America

**E** VERY job in Production for Victory calls for top visual efficiency. Without concession to time, place or condition, work must go on. This means that eyes must function unfailingly and unflinchingly—at lathe, bench and on assembly line, in research and control laboratory, over drafting board and foundry flask.

Upon the shoulders of the nation's eyesight specialists, rests the responsibility of forestalling eyestrain as an unconscious saboteur.

As a maker of ophthalmic products-

the instruments used in the scientific examination of the human eye, the spectacle lenses, frames and rimless mountings which these specialists use— Bausch & Lomb has an important part in America's war effort.

In the development and manufacture of actual fighting equipment, such as rangefinders, aerial height finders, binoculars, aerial map-making equipment, Bausch & Lomb is serving the Armed Forces directly. At the same time, Bausch & Lomb is providing the metallographic equipment, the microscopes, spectrographs, contour measuring projectors, optical glass and special instruments required by other manufacturers in filling military needs.

The ideals, ability and resources which have made the name of Bausch & Lomb a symbol of precision and scientific integrity for 89 years are concentrated upon America's job at hand.

#### BAUSCH & LOMB OPTICAL COMPANY • ESTABLISHED 1853

DDUCING OPTICAL GLASS AND INSTRUMENTS FOR MILITARY USE, EDUCATION, RESEARCH, INDUSTRY AND EYESIGHT CORRECTION



# EXPERIENCE WITH PROBLEMS LIKE YOURS ENABLES SWENSON ENGINEERS TO DESIGN THE BEST FILTER FOR YOUR SPECIAL JOB

In designing filter equipment for a particular application, Swenson engineers not only know what to do—but what NOT to do, which is even more important! Through experience as well as craftsmanship, they are qualified to provide the most satisfactory filters for any given set of conditions.

#### **Technical Background**

Superior technical ability in the design and fabrication of chemical equipment is combined at Swenson with complete manufacturing facilities. Swenson engineers personally supervise and control the construction of each individual unit.

#### **Diversified Experience**

The policy of making periodic check-ups of Swenson installations has given Swenson engineers intimate knowledge of the performance of filters under a wide variety of operating conditions. When designing new equipment, they are not limited to theory and empirical formulas . . . they can draw from actual experience with similar problems.

#### **Extensive Research**

For many years Swenson has conducted a continuous program of research and development, which has proved a most valuable source of information. Swenson engineers have this data at their fingertips when designing equipment for unusual applications. Many instances can be cited to show how this program has been of important benefit to Swenson customers.

#### Swenson Five-Way Service

Swenson does more than build chemical equipment. Swenson service covers every detail from the analysis of individual requirements to test operation and periodic check-ups of performance.



The Swenson Top Feed Filter dewaters and dries in a single operation. It is particularly suited to the filtration of magmas containing crystals so coarse or heavy they cannot be maintained in uniform suspension. In operation, the Swenson Top Feed Filter is noted for its high capacity, high thermal efficiency, and low operating cost.

#### SWENSON EVAPORATOR COMPANY Division of Whiting Corporation

15671 Lathrop Ave.

Harvey, Ill.

#### ONLY SWENSON PROVIDES THIS FIVE-WAY SERVICE

1. Analysis of Requirements







4. Test

Operation

Check-ups

00

5. Periodic



#### INDUSTRIAL AND ENGINEERING

# VICTOR OVER ACID VAPORS

Acid fumes which are created during one of the stages in the production of rare metals, such as tungsten and tantalum, constitute an operating hazard. During the agitation and precipitation periods in the process, these fumes are given off in volume.

At the plant illustrated, process fumes are vented from the reaction vessels by means of a rubber-lined duct system to four Schneible Multi-Wash Collectors. These collectors are of standard steel construction and have a total capacity of 125,000 c.f.m. The washing medium used to neutralize and collect the fumes is a caustic soda solution. which reacts on the acid vapors so that all nuisance is eliminated. The alkaline solution at the same time thoroughly and continuously washes the interior of the collector. preventing corrosion. As the fans are located on the exhaust side of the collectors, they are of course protected from the corrosive vapors.

#### THE SCHNEIBLE SENIOR MULTI-WASH COLLECTOR

The Multi-Wash Collector has proved its effectiveness in cleaning the air and improving working conditions in many processing plants. This unique method removes fumes and odors, as well as dust from the air, thoroughly cleansing the air before it is exhausted to preclude a plant or neighborhood nuisance. The towers are built of the metal best suited to resist the particular dust and fumes encountered, and are made in capacities up to 30,000 c.f.m. and in multiple unit installations. Settling and dewatering equipment provides for water or washing liquid being used over and over again and, where valuable dusts are collected, they can be recovered.

Whether your dust and fume problem covers your entire plant or a single troublesome operation, Schneible engineers will gladly work with you toward its solution.

 CLAUDE B.
 SCHNEIBLE
 COMPANY

 3959 LAWRENCE AVE.,
 Offices in Principal Cities
 CHICAGO, ILLINOIS



# Automatic Prepared Monthly by U. S. Industrial Chemicals, Inc. Image: Control of the structure of the Solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries Image: Control of the solvents and Chemical Consuming Industries <th Image: Control of the solvents and Chemical Co

#### New Acetone Uses Indicated by Study Of Patent Files

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Chemical Plays Important Part In Processes in Varied Fields

A search of the patent files reveals many new uses for acetone in a number of varied fields, somewhat of a surprising fact because acetone has generally been considered a staple chemical with a fairly well-defined field of utility. A discussion of a few of these patents may serve to indicate the variety of hitherto unexplored applications of acetone.

One such patent concerns the concentration or recovery of the values of non-metalliferous ores by froth flotation processes in which fatty acid substances are employed as promoters. The inventor states that the power of the promoters can be very greatly increased by dilut-(Continued on next page)

## Reactions Show Possibilities of Ethyl Sodium Acetone-Oxalate

Versatility Clearly Indicated by Formation of Ring Compounds

A study of the reactions of ethyl sodium acetone-oxalate, a compound having the formula  $CH_3COCH = C(ONa)COOC_2H_5$ , shows many new interesting possibilities.

The versatility of this chemical or the acid derived from it, alpha, gammadioxo-valeric acid, or its esters, in the formation of ring compounds may be seen

#### Ethylene Used as Alkylator To Produce Anti-Knock Gas

CHICAGO, Ill. — A method for alkylating isobutane by ethylene in the presence of a particular type of catalyst to produce a motor fuel of relatively high anti-knock value has been developed by two men here, according to a patent that was granted recently.

from the table below. The first line of the table, for instance, shows that hydrazine reacts with ethyl sodium acetone-oxalate to give 3-methyl-5-pyrazolecarboxylic acid. One reaction not included below is that of ortho-aminobenzaldehyde, which is reported to produce a quinoline derivative,  $C_{11}H_{11}O_{1N}$ , whose structure has not been completely elucidated [Monatshefte für Chemie 52, 59-67 (1929)]. Samples of ethyl sodium acetone-oxalate may be obtained from U.S.I. on request for experimental work.

#### ETHYL SODIUM ACETONE-OXALATE $CH_3COCH = C(ON_a)COOC_2H_5$

RING COMP	OUNDS	SUBSTITUTED GROUPS	REAGENT	REFERENCE					
	H	3-methyl; 5-carboxylic acid	HYDRAZINE	Knorr A.279,217 (1894) German Patent 74,619,F.3,938					
PTRAZOLE	HĆs <sup>'</sup> zN HC <u>4</u> CH	3-methyl; 1-phenyl; 5-carboxylic acid 5-methyl; 1-phenyl; 3-carboxylic acid	PHENYLHYDRAZINE	*Claisen & Roosen A.278,279,288 (1893)					
ISOXAZOLE	0 HCs <sup>1</sup> 2N HC⁴_3CH	3-methyl; 5-carboxylic acid 5-methyl; 3-carboxylic acid	HYDROXYLAMINE	°Claisen, B.24,3908 (1891)					
	Н	2,3-dioxo; 4-acetyl; 1,5-diphenyl	BENZALANILINE	Schiff, Gigli, B.31,1307 (1898)					
PYRROLIDINE	$H_2 C_5 ^{1} C_2 H_2$ $H_2 C_2 ^{4} C_2 H_2$	4,5-dioxa; 1-methyl; 2-phenyl; 3-acetyl	BENZALDEHYDE & METHYLAMINE	German Patents 280971, 283305,290531 F.12,792, 793,797					
PYRROLE	H HCs 2CH HC4 3CH	4-methyl; 3-acetyl; 2-carboxylic acid	AMINOACETONE	Piloty, Blömer B.45,3752 (1912) Fischer et al., A.461:244 (1928)					
1,3-DIOXOLANE	$H_2C_5 \xrightarrow{2} CH_2$ $H_2C_4 \xrightarrow{3} O$	4-oxo; 2-trichloromethyl; 5-acetyl methylene	CHLORAL	Schiff B.31,1305 (1898)					
	10	2,3-dioxo; 4-acetyl; 5-phenyl	BENZALDEHYDE in piperidine	Ruhemann J.C.S.89 1239,1240 (1906)					
OXOLANE	$H_2 C_5 \ ^2 C H_2$ $H_2 C_4 \ ^3 C H_2$	2,3-dioxo; 5-phenyl; 4-cinnamoyl BENZALDEHYDE dried HCl		** ** **					
		3-methyl: 5-hydroxy; 1-carboxylic acid	BARIUM HYDROXIDE	Claisen B.22,327 (1889)					
BENZENE	6 2 5 3	5-methyl; 3-hydroxy; 2-ethoxalyl; 1-carboxylic acid	SODIUM ACETATE	C.A. 32,3340 (1938)					
	N	4-methyl; 3-acetyl; 2,6-dicarboxylic acid 4-methyl; 3-acetyl; 6-carboxylic acid 4-methyl, 5-acetyl; 2-6-dicarboxylic acid	AMMONIA AMMONIA AMMONIA	Mumm, Bergell B.45,3045 (1912) C.A. 26 2171 (1932)					
PYRIDINE	5 3	2,6-dimethyl; 3,4-dicarboxylic acid	ETHYL B-AMINO- CROTONATE	Mumm & Hunecke B.50,1573 (1917)					
*See also B.45, 3045 (	1912). Abbreviations:	A. — Liebig's Annalen: B. — Berichte der Deutschen Fortschritte der Theerfarben Fabrikation; J.C.S. – J	Chemischen Gesellschaft; C ournal of the Chemical Socie	A. — Chemical Abstracts; F. — Friedlaender, ty.					

January

# **U.S.I. CHEMICAL NEWS**

#### **Many New Chemical Developments Noted During the Past Year**

\*

An idea of the outstanding chemical progress made during 1942 can be gained by a brief review of the major developments summarized in the past year's issues of U.S.I. CHEMICAL NEWS, During 1942 the following topics were discussed in leading articles in this publication:

January. Reactions of urethan. Unusual possibilities of alkyl phosphates.

February. Importance of water in resin solutions. Use of chemicals in lengthening the life of fish nets.

March. Applications of ethyl benzoylacetate in dye manufacture and chemical synthesis. Luminescent finishes.

April. Ethyl carbonate as a raw material. Lined steel drums.

May. Possibilities of ethyl acetoacetate.

Novel experimental vinegar generator. June. Determination of the combined acids in cellulose mixed esters. New chemical to end corrosion of iron by lacquers.

July. Utility of ethyl sodium oxalacetate in chemical synthesis. Ethyl formate for treating varns.

August. Carbon dioxide as a fire extinguisher and inflation agent. Availability of ethyl sodium acetone-oxalate for experimental work.

September. Resin emulsions as possible latex substitutes. Novel perfumes from Indian plant lore.

October. New method for studying drying rates of lacquer films. Use of heat treatment in improving quality of yellow pigments. November. Preparation of ethyl oxalace

tate. Puerto Rican plants yield essential oils. **December.** The prevention of foam in casein paints and other protein compositions.

Procedure for improving synthetic camphor yield.

(Copies of these issues are available on request)

#### Varnish for Maintaining **Sterile** Operative Field

A new skin varnish for maintaining sterility in the operative field has been developed according to the following formula:

Santicizer	·B				 •					•		•	×,	. 16.5 g.
Acetone .		• •							•	•	•			.605
Ethyl cell	ulo	se							•	•	•			.165
Ethanol .				• •						•	•			.715
Castor oi	۱.													. 16.5

#### Tests Show Superiority of **Ethanol as Disinfectant**

Ethanol is considered to be an ideal disinfectant, according to experiments in which the effect of ethanol in adsorption tests, particularly in the disinfection of hands, was studied.

One of the special advantages claimed for ethanol is its capacity to kill large numbers of bacteria. It was discovered that when two loopfuls of solid growth of staphylococci or B. coli are suspended in only two drops of 96% ethanol, complete disinfection takes place in a few minutes, whereas 1% Zephirol, 5% Sagrotan and 0.1% mercury solutions fail to achieve this.

#### **New Acetone Uses** (Continued from previous page)

ing the flotation reagent with about 20% or less of a water-soluble ketone such as acetone.

Another patent of interest involves the preparation of sulfanilylamino-pyridine com-pounds. A mixture of acetone and pyridine is used to form a reaction medium for reacting p-acetylaminobenzene sulfonyl chloride with alpha amino pyridine for the production of 2-acetylsulfanilylamino-pyridine.

#### **Printing-Ink Binders**

Rapid drying properties, high gloss and water-insolubility at slightly elevated temperatures are among the advantages claimed for the use of acetone-formaldehyde resins as binders for printing inks. The formation of such an agent comprises interacting formaldehyde with acetone in the presence of an alkaline catalyst, pigmenting material, and a liquid organic solvent such as acetone.

In another patent, acetone is suggested in combination with nitrocellulose to form an adhesive for use in holding metal parts to be welded into position, such as threaded steel buttons to a background of steel ship plates.

A more simple method of producing al-cohols of the acetylene series than those now in use is claimed in a recent patent. Such alcohols are prepared directly from acetone and acetylene by bringing into contact acetylene with a mixture of acetone and an aqueous solution having an alkaline reaction.

Acetone is also suggested by an inventor for the manufacture of beta-cyanoacrylic acid esters. According to this process, such esters are obtained by reacting an ester of alpha-chloroacrylic acid with a cyanide of an alkali metal or an alkaline earth metal at approximate room temperature in the presence of water and acetone.

#### TECHNICAL DEVELOPMENTS

#### Further information on these items may be obtained by writing to U.S.I.

A moistureproof sealer particularly developed to seal waterproof papers used as liners in shipping containers is said to even protect goods against immersion. A white, colorless fluid, the adhesive seals overlapping liner seams against air, mois-ture and temperature extremes. (No. 650) U S I

A liquid temperature indicator employing the same principle as pellets and sticks is intended for use in signalling temperatures. It is available in melting points from 125 to 1600° F. When ap-plied, it dries instantly, then liquefies sharply when the desired temperature is reached. (No. 651) (No. 651)

USI

USI a grease-impervious paper box for packaging ointments and similar substances is offered, which has an outside covering of parchment paper supplementing the chemical compound which coats the inside. Although not impervious to water and grease in the same degree, it is said to successfully package substances which have a water content up to 5%. USI A protective paint is offered for exterior and in-

A protective paint is offered for exterior and in-terior surfaces having an appreciable amount of exposed metal. The primers are said to be rust inhibitive and provide a tough, elastic film which expands and contracts at the same rate as the metal. (No. 653)

USI Citric acid substitutes are now being produced domestically by a manufacturer who made similar products in Europe during the last World War. (No. 654)

USI A prepared catalyst for isomerization processes has been developed, consisting of activated baux-ite impregnated with 15 to 20% of anhydrous aluminum chloride. (No. 655) USI

Non-ionic emulsifiers are available commercially which are said to offer very interesting possibil-ities in the manufacture of synthetic rubbers by polymerization of butadiene, styrene, acrylonitrile or other unsaturated compounds. (No. 656) U S I

USI static-conductive lineleum is offered which is de-scribed as nonsparking and highly conductive of static, yet providing adequate protection against accidental grounding from service charges. It is said to meet Ordnance Department specifications for floor and table coverings in explosives opera-tions. (No. 657) USI

A new colorimeter of the continuous-flow type is offered, which is said to permit the determination of light transmission of a liquid passing through the instrument. Its application, therefore, is sug-gested for the continuous control of chemical processes in which the color or turbidity of a liquid must be checked as an indication of con-centration or other property. USI

Paint brush bristles have been developed from Nylon which are not only said to have the re-quired taper, but also resiliency, toughness, length and inertness to paint ingredients. At present their use is being restricted to military purposes. (No. 659)



PHTHALIC ESTERS Amyl Phthalate Butyl Phthalate Ethyl Phthalate

Acetoacetanilide Acetoacet-ortho-anisidide Acetoacet-ortho-chloranilide Acetoacet-ortho-toluidide Acetoacet-ortho-toluidide Acetoacet-para-chloranilide Ethyl Benzoylacetate Ethyl Benzoylacetate Ethyl Sodium Oxalacetate

Registered Trade Mark

\*Vacatone

#### 1943



AW-KNOX

builds complete

**Process** Plants

Cracking

#### BLAW-KNOX DIVISION OF BLAW-KNOX CO

From Idea to

Operation

2081 FARMERS BANK BLDG., PITTSBURGH, PA. **Offices in Principal Cities** 

Complete plants or equipment for the following processes . Kilning and Calcining **Organic Synthesi** Distillation Emulsification **Gas** Absorption Polymerizing ' High Pressure Solvent Extraction Solvent Recovery Evaporation Processing Crystallization Impregnating **Heat Transfer Gas** Cleaning Drying Furnacing **Mixing and Stirring** and others :

DOUBLE REAL COM COMPANY OF THE COMPANY HERKINGDOVE CLAM SPEED REDUCER Straight Line Drive

MOTORIZED PLANETARY CELL SPEED REDUCER Herizental and Vertical Types

# D.O. BREDUCERS

MOTORIZED HELICAL GEAR

HEAVY DUTY WORM GEAR SPEED REDUCER Type H-Horizontal Type

HALF CENTURY MAKERS OF

DOUBLE WORM GEAR SPEED REDUCER Shaft Extended Upward

TORIZED WORM GEAR SPEED REDUCER Horizontal Type

FOR OVER A

RIGHT ANGLE SPIRAL BEVEL PLANETARY GEAR SPEED REDUCER PLANETARY GEAR SPEED REDUCER

DOUBLE WORM GEAR SPEED REDUCER Horizontal Type

1888

#### THEY JUST KEEP ROLLIN' ALONG

The precision-in-built quality and design of the D. O. James Speed Reducers gives them a formidable achievement record that has definitely proven Established the statement that they are "built to take it." Now, more than ever, this is an imperative quality—and will vitally aid in the maintenance of American Industry's War-Time Production Schedules — "That Must Be Kept Rollin' Along!"

D.O. JAMES MANUFACTURING COMPANY CHICAGO, U. S. A. 1140 W. MONROE STREET ۲

EVERY TYPE OF GEAR AND GEAR REDUCER

HELICAL WORM GEAR SPEED REDUCER Vertical Type

HELICAL WORM GEAR SPEED REDUCER Horizontal Type

TRIPLE REDUCTION CONTINUOUS-TOOTH HERRINGBONE GEAR SPEED REDUCER

MOTORIZED WORM GEAR SREED REDUCER

CONTINUOUS-TOOTH HERRINGBONE GEAR SPEED REDUCER Single Reduction

Vol. 35, No. 1

# **Robot Chemists!**



These robot chemists have just been drafted to guard the process cooling and heating sys-tem of one of our most vital war plants. Sorry — no names, dates, places, at this time. But here's what these Solu-Bridge Controllers do in this one specific application:

During normal operation of acid coolers, these instruments are inactive though constantly on guard. But when acid enters guard. But when acid enters system from any cause, the electrical conductivity of water in-creases. Set for given danger point, the Solu-Bridge Controller sounds alarm while panel light changes from green to red. Also, solenoid pilot valves are ener-gized, admitting water under pressure to hydraulic cylinders of line valves, opening line to

acid waste system and closing the line of the recirculating system.

24 hours per day, 168 hours a week, Solu-Bridge Controllers stand guard over vital pipe lines and processes. Without overtime premium, with only routine inspection, such equipment will:

spection, such equipment will: 1. Check cooling water continuously for contamination. 2. Flash alarm. 3. Operate solenoid valves diverting con-taminated water to waste. 4. When leakage or contamination cesses, normal operating conditions automatically re-stored. 5. Provides means of measuring dissolved solids in cooling water. 6. Shows by pilot light that system is operative. 7. Should instrument for any reason become inoperative, water will be diverted to waste and warning given. given.

This is a typical usage. Such equipment is solving manpower shortage and speedup in many chemical plants these days. Why not apply it to your situation?



MANUFACTURED BY



HOW IT WORKS

• This is the standard Solu-Bridge Controller. Modifications meet the more unusual requirements.

An electronic device utilizing electronic tubes and self-contained relays for control of warning signals and corrective means. Wheatstone Bridge circuit, independent of line voltage and variation in tube characteristics.

Main dial set to give electrical conductivity value. Can be calibrated in any required terms. Second dial set to average operating temperature. General wiring scheme shown at right.

When conductivity exceeds set limit, controller operates warning or corrective means, auto-

Moderate cost. tually foolproof

Industríal

Instruments

# ORROSIVE SOLUTIONS

#### DURCOPUM

Wet end parts Durcopumps an infinite num ber of corrosid resisting alloy all strictly int changeable.

The fact that the wet end parts of Durcopumps are interchangeable is important at all times — but especially so if there are apt to be changes in your manufacturing processes.

Full scale production may vary from pilot plant operation. Or perhaps your peace-time products will utilize different corrosive solutions from your present war products. Your Durcopumps can be converted to correspond with the changes in the acids or alkalis they handle.

If you are using Durcopumps now, you are assured continued operation by

PURIRON CO., INC.

using available materials, converting to the optimum at a later date.

The point is that Durcopumps furnished now in the high-silicon irons, *Duriron* and *Durichlor*, can be converted later to any stainless steel, or any other machinable alloy. Likewise, the reverse is true.

If you need pumps for handling corrosive solutions up to 2000 gpm. we urge you to get our Bulletins Nos. 810-D and 811-C at once. They will show in detail the exceptional and exclusive advantages offered in the new Model 40 Durcopumps.

DAYTON, OHIO, U.S

INDUSTRIAL AND ENGINEERING CHEMISTRY

VUI. 00, .... -



In 1925, anticipating the requirements of the fast growing Chemical and Process Industries, Powell pioneered in producing an entirely new type of valve—the Corrosion Resistant Valve.

Today, Powell has a complete line of valves designed for long, unfailing service in the exacting control of the innumerable corrosive media.

Naturally the Powell Line has been simplified and standardized as far as possible, but a considerable diversity of design is necessitated by the limitations of the materials from which the various valves can be produced. However, each valve is designed to meet the requirements of a number of different services.

Shown here are a few examples of Powell's Corrosion-Resistant Line.







29



Foster Wheeler has engineered and built many large selective and non-selective catalytic polymerization plants and associated processing equipment charging gas or liquid fractions or both.

Foster Wheeler is prepared to convert these plants or engineer and build new plants for the petroleum war industry to produce;

- **1.** ETHYL BENZINE for STYRENE, important constituent for synthetic rubber.
- 2. CUMENE FOR 100 plus octane rich mixture aviation fuel.
- 3. CODIMER which is dehydrogenated for high octane aviation fuel component.

FOSTER WHEELER CORPORATION, 165 BROADWAY, NEW YORK, N. Y.

FOSTER W WHEELER

INDUSTRIAL AND ENGINEERING CHEMISTRY

# NO TIME TO LOSE

30

IN back of the fighting lines, on the home front, Marblehead Chemical Lime is doing its own yeoman job of helping to save manhours of time, rolling up production records, making it easier and safer for lime users to keep their tight delivery promises.

# MARBLEHEAD High Calcium CHEMICAL LIME

MARH FHEAD

LIME CO.

Marblehead is chemically and physically fit to respond to these new and tougher demands, because it has been in training for over half a century in all kinds of peace-time industries, on the hardest sort of jobs. The same high calcium chemical energy, purity, fine physical qualities and consistent uniformity, now serve the war industries just as efficiently and dependably.

Calcined in modern rotary kilns and handled and processed throughout with expert care and precision, Marblehead high quality, high calcium

160 N. LaSalle St.

Chicago, III.

limestone becomes the outstanding chemical lime in the field — truly a chemical product.

In Service for Over Half a Century for STEEL MAKING -- WIRE DRAWING --PAPER AND BOXBOARD-LEATHER-PAINT AND VARNISH-BRICKS -- CHEMICALS -- FOOD PRODUCTS -- WATER TREATMENT, ETC.

YOUR OWN PLANT

FOUR FORMS

LIME

A CAR NOW IN

TRY

# How Calgon helps speed America's war effort: 4. IN THE ORDNANCE PLANTS

THE things that Calgon does well in the normal industry of peace time it is doing just as effectively in the ordnance plants under the hard drive of war-time necessity.

Maximum production demands, continuous operation at peak capacity and shortages of materials are presenting serious problems to the men responsible for America's war production.

Wherever water is involved, Calgon is doing double-duty in the ordnance plants, helping to maintain maximum capacity of condensers, heat exchangers and water distribution systems, with a minimum of breakdown and replacement.

If Calgon had been expressly created to help you in this emergency, it could not have been better designed for the task. Condensers and heat exchangers can be kept up to capacity because Calgon fed to the cooling water at the rate of 1 to 5 ppm. inhibits the deposition of calcium carbonate scale. Water distribution lines can be maintained at maximum capacity, year in and year out, because 1 to 5 ppm. of Calgon prevents calcium carbonate scale, 2 to 10 ppm. controls corrosion.

If you are not familiar with the many properties of Calgon,\* and the simplicity of its application, write for a free sample and a copy of the Calgon Data Book. Our Calgon specialists will be glad to provide further detailed information for the solution of any specific problem.

\*Calgon is the registered trade-mark of Calgon, Inc. for its glassy sodium phosphate products.



# LET'S GET IN THE SCRAP -but not make it!

### "Piping Pointers" Show You How To Reclaim Valves

THE steel mills need all the scrap they can get. But, first salvage all readily usable equipment when practical. Every reclaimed valve, for example, means that another new one is available for essential war industry—that another valve is on hand to keep production lines flowing. For practical, valuable hints on reclaiming valves, get a copy of this Crane "Piping Pointers" Bulletin No. 5.

#### "Piping Pointers" Free on Request

"Piping Pointers" Bulletins help you do three important wartime jobs: (1) Train new men for piping TO GET BETTER AND LONGER SERVICE FROM VALVES!



FOR VICTORY'S SAKE

CRANE VALVES

BAR 18 REFER BILL IN COMPANY AND REFER BI WAT

Crane Co., 836 S. Michigan Ave., Chicago, III.

IT'S OUR DUTY

TO KEEP YOUR

How to Repair Valves

14

Z 10

L

Handles Acids Corrosives

Hot Liquids Mild Abrasives

at a LOWER COST

INDUSTRIAL AND ENGINEERING CHEMISTRY

FOR INCREASED PRODUCTION WITHOUT INTERRUPTION

# Record-Breaking **TROUBLE-FREE** PERFORMANCE

Wherever record-breaking, trouble-free handling of acids, corrosives, hot liguids, mild abrasives, etc., is important, more and more plants are turning the whole job over to WILFLEY Acid Pumps. That's because the WILFLEY gives continuous - or intermittent - performance 'round-the-clock without attention. That means increased production ... lower costs. Capacities: 10- to 2,000-G.P.M. Heads: 15- to 25-ft. and higher. No stuffing box ... therefore no stuffing box trouble. No rubbing contact . . . effective sealing blades eliminate leakage problem. Individual engineering service. Write for complete details.

A. R. WILFLEY & SONS, Inc., Denver, Colorado, U.S.A. NEW YORK OFFICE: 1775 BROADWAY, NEW YORK CITY



# STURTEVANT MACHINES designed for 24 hour service

Designed and built to operate continuously day in and day out without failures or shut-downs, Sturtevant Machines, and units made up of Sturtevant Machines, are "tops" with practical operators all over the United States.

Custom-made in the sense that each one is built for a specific predetermined service, with a quality and capacity equalling the mechanism preceding or following, Sturtevant machines are tailored to fit and assembled in the shop to avoid errors and to save erection costs in the field.

On this page are a few of the Sturtevant machines most in demand today.

#### **RING-ROLL MILLS**



For medium and fine reduction (10 to 200 mesh) hard or soft materials. Very durable, small power requirements. Operate in closed circuit with screen or Air Separator. Open door accessibility. Many sizes, large or small capacities. No scrapers, plows, pushers or shields.

#### DRY BATCH MIXERS



These are Batch type mixers for intimate blending. One opening takes care of intake and discharge. Open door accessibility. Many sizes, 1/4 to 2 tons—Large outputs. Simple, Compact, Easy Running, Practically Dustless. With or without hoppers. Also Dustless Batch Blenders.

#### SWING SLEDGE MILLS



For coarse and medium reduction. (1" to 20 mesh.) Open door accessibility. Soft, moderately hard, tough or fibrous substances. Built in several types and many sizes.

#### **CRUSHING ROLLS**



For granulation, coarse or fine, hard or soft materials. Precision and automatic adjustments. Crushing shocks balanced. For dry or wet reduction. Sizes 8 x 5 to 38 x 20. Roller or Plain Bearings. The standard for abrasives.

STURTEVANT MILL CO. <sup>2</sup> HARRISON SOUARE

#### AIR SEPARATOR



Operated in a closed circuit with the pulverizer, the Sturtevant Air Separator increases outputs from 25 to 300%, effecting power savings of 10 to 50% . . . Compact and rigid construction, easy adjustments, and large feed openings are special features of its design. Built in many sizes from 3 to 18 feet in diameter for capacities ranging from 1/4 ton to 50 tons per hour. Efficiently handles all materials within a 40-350 mesh range of

#### **ROTARY CRUSHERS**



For intermediate and fine reduction. (1" to <sup>1</sup>/4".) Open door accessibility. Soft or moderately hard materials. Efficient granulators. Excellent preliminary Crushers preceding Pulverizers. Many sizes. Belt or Motor driven.

#### LABORATORY MACHINES



A complete line of small size machines with the strength of full size equipment. Jaw and Rotary Crushers, Rolls, Hammer Mills, Disc Pulverizers, Screens, Air Separators, Coal Crusher and Sampler, Vibrating Test Sieves.

BOSTON, MASS.



#### It's already Day after Tomorrow!

Under the stinging lash of a war for survival, American chemists are fighting fantastic battles . . . cramming a year's progress into a day . . . drawing up, in advance, the pattern of things to be.

For this is the new, stupendous era of synthetics. Already scientists are talking about glass that will float, wood that won't burn, window screens without wire, machinery bearings without metal.

Badger—with its engineers, chemists, draftsmen, designers, construction workers—is helping in this effort to save America now, to enrich her later on. Among its many war jobs, Badger is building plants and equipment for the manufacture of butadiene and other materials required to make artificial rubber. It is building plants for producing acetic acid and phthalic anhydride used in the manufacture of plastics for airplanes. It is building plants for the manufacture of T.N.T. It is erecting huge refineries for the production of high-octane aviation gasoline.

Miracles are being performed in the petro-chemical industries today. For obvious reasons, they can't be talked about in detail. But they do send this message to every American: Win this war—and the dawn will break on a world more wonderful than you have ever known.



PROCESS ENGINEERS AND CONSTRUCTORS FOR THE PETRO-CHEMICAL INDUSTRIES



Electro-Chemograph in operation, testing for Fe and Al. The two curves on the chart show two Al solutions of different concentration.

# METALLIC ELEMENTS DETERMINED With ELECTRO-CHEMOGRAPH

Application of the dropping-mercury electrode method to the determination of metallic elements present in a solution has been successfully worked out with an Electro-Chemograph by a member of the Geology Department at Bryn Mawr College.

Analyzing for Fe and Al in particular, the scientist shown above obtains qualitative and quantitative results in one operation. The Electro-Chemograph automatically records, on its potentiometer-type Micromax Recorder, the current and potential curves which identify and quantitatively indicate the presence and concentration of a given element. The time of analysis is only a fraction of that required by other standard methods; the exact speed depends largely on the specimen to be determined; and on the experience of the user.

Bibliography E-94(1), listing 825 papers on the dropping-mercury electrode method, and Technical Publication E-94(1), will be sent on request.

Jrl Ad EN-0880(3)



L&N Glass-Electrode pH Indicator

#### pH Indicator for Labs & Plants

Adjustment of pH is a necessary corollary to Electro-Chemograph determinations of Fe and Al, and the instrument we usually recommend for pH checking of this sort is our Glass-Electrode pH Indicator.

This Indicator is especially intended for fast, accurate work in control and research labs. It reads directly in pH, to a limit of error of only 0.1 pH; it is self-contained, and can be used for titrations as well as for pH. Outstanding characteristics include:

1. Full accuracy is retained in atmosphere of 95% relative humidity up to 85 F. 2. Electrodes are sealed and filled at factory.

3. Entire instrument is electrically shielded; won't be affected by outside electrical conditions.

4. Solid mahogany case, special finish, separate battery-compartment, heavy hinges and many other construction features make this a strong, dependable, lasting equipment.

For further details, see Catalog E-96(2).



Admiral Henry A. Wiley, with Factory Manager W. R. Coley of L&N, pauses for a word with an L&N girl-employee at time of Army-Navy "E" Award to L&N.

"E" for L&N

The Army-Navy E was awarded to the Leeds & Northrup Co. on September 5, in ceremonies featured by the presentation of the "E" Burgee to the organization as a whole, and the authorization of "E" Pins to its members.

Admiral Henry A. Wiley praised the Company's attitude, and the results it has produced. President C. S. Redding of L&N, joined by spokesmen for L&N employee groups, pledged continued increases in production. The Company's output consists of classified materiel, in addition to its established lines of instruments, telemeters, automatic controls and heat-treating furnaces.

William L. Batt, Vice-Chairman of W.P.B., voiced the Board's pleasure at having the achievements of Industry so recognized by our armed forces.



# ACCORDION-IYPE STEEL EXPANSION JOINT in RECTANGULAR PIPING used in an Ore Mill

#### **JAY-CEE PRODUCTS**

ALUMINUM PLANTS Hoppers & Chutes Stacks & Breechings Annealing Baskets Special Machinery

POWDER PLANTS Tanks Pressure Vessels Fabricated Piping Special Machinery

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The "Jay-Cee" organization is particularly well equipped and trained to build unusual equipment in iron and steel for the Process Industries. You may have a problem right now which "Jay-Cee" technicians and craftsmen can

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solve, for you, as they have for large and small organizations for nearly 60 years.

If it's made of iron or steel, draw a picture of it and "Jay-Cee" will build it for you. Inquiries entail no obligation.

JOHNSON CITY FOUNDRY & MACHINE WORKS JOHNSON CITY, TENNESSEE EST. 1883 GRAY IRON and ALLOY IRON CASTINGS - STRUCTURAL STEEL - MISCELLANEOUS and ORNAMENTAL IRON WORK - SPECIAL MACHINE WORK



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# from CARBIDE AND CARBON CHEMICALS CORPORATION

# Literature **That Contains Useful Information**

S part of our service to industry, we publish literature describing the properties and uses of the synthetic organic chemicals we make. Five books from this literature are listed and briefly digested below. If any of these are directly useful in your work, you can get a copy by asking for it on your company letterhead. Please refer to the form number in your request.



Glycols . . . includes the names, formulas, properties, and uses for the glycols produced by Carbide and Carbon Chemicals Corporation. Numerous graphs on physical properties and a bibliography are also included. 20 pages.  $8\frac{1}{2}$  by 11 inches. Form 4763



PRODUCERS OF SYNTHETIC

Organic Acids . . . is similar to the "Glycols" booklet and includes the names, formulas, properties, and uses of the acids we make, as well as graphs illustrating the physical properties. 12 pages.  $8\frac{1}{2}$  by 11 inches. Form 4768



Synthetic Organic Chemicals . . . includes the names, formulas, properties, and uses of all the chemicals we make in commercial quantities. This is the eleventh edition of this manual of synthetic aliphatic organic chemistry, and incorporates some minor revisions. 100 pages. Form 4372A  $8\frac{1}{2}$  by ll inches.



Chemicals Available in "Research" Quantities ... gives information supplementing the "Synthetic Organic Chemicals" book on 32 new "research" chemicals announced this year. It includes a table of physical properties of the products we make. 16 pages. 81/2 by 11 inches.

Form 5298



Solvent Recovery by the "Columbia" Activated Carbon System . . . describes the "Columbia" activated carbon system of solvent recovery and explains its profitable applications. Other useful applications of "Columbia" activated carbon are also briefly described. 32 pages. 81/2 by Form 4410 11 inches.

#### **Other Information**

Loose-leaf data sheets . . . including graphs of physical properties . . . are available for many of the 160 synthetic organic chemicals produced by Carbide and Carbon Chemicals Corporation. Ask for those in which you are interested.

ORGANIC CHEMICALS








### HARRISON ESTELL HOWE, 1881–1942

His work is an enduring monument His spirit marches on.

H11100.5

"Write his name as one who loved his fellow man"

#### A Message from Our President

**I**N SENDING a cordial New Year's Greeting to the 32,000 members of the AMERICAN CHEMICAL SOCIETY, your incoming President appreciates that he is taking office at a time when we are confronted with many unusual tasks and problems.

One of the questions of greatest concern to our membership is how to provide the necessary technical personnel for the war effort. Although some industries may be in a position to release technically trained men for more essential work, any such gain is more than outweighed by the necessity on the part of other industries to expand their research, development, and manufacturing programs at an unparalleled rate. In the midst of this we are faced with a dwindling supply of new graduates, a situation which, in turn, threatens the very existence of our system of higher education.

There has never been any real dissension concerning the necessity of providing an adequate supply of technically trained manpower for the furtherance of the present war effort. The Director of the Selective Service System has recognized this principle in his directives to the local draft boards, and Secretary of War Stimson was recently quoted in *Chemical and Engineering News* as follows:

The Army is greatly in need of men of specialized training, particularly in physics, chemistry, engineering, and medicine. We are equally interested in having adequate numbers of men of such training available to war-production industries and civilianresearch agencies of the Government.

So far, the universities and industry have depended on solving their part of the problem by recourse to deferment under the Selective Service System. This approach has by and large produced satisfactory results. The Secretary and Business Manager of the AMERICAN CHEMICAL SOCIETY has done much to clarify the policies involved, and the cooperation received from the great majority of local draft boards has been most gratifying.

The technical manpower problem is now, however, entering into a new phase caused by the efforts to build a Combat Army beyond the limits made possible merely as a result of the recent lowering of the draft age. It is becoming increasingly difficult to keep men in civilian jobs, particularly so in the case of younger and unmarried men. Let us hope that the situation will be clarified to a point where it will be possible to permit technically trained men to continue doing essential war work. If not, immediate and forceful action will be called for to obtain a clear-cut ruling in the matter. As a profession we do not want class deferment. But, technically trained men already doing essential war work in industry, or capable of filling such jobs, must not be drafted for nontechnical service.

There is no way of telling how long the war will last. However, even those who believe that it will be over soon, will agree that our planning must be on a longterm basis. That leads to the question of future supply of graduates. With respect to this point, there is an urgent need for the establishment of a definite policy. We can ill afford hesitation here. If action is delayed only long enough to interfere seriously with an orderly program for this year's enrollment in our colleges and universities, the damage done may be too far flung in its consequences for ready repair.

In spite of all efforts to replace men with women wherever possible, it seems imperative that at the age of 18 a certain number of boys will have to be selected for enrollment in our institutions of advanced learning. After even one semester a further selection can be made, at which time some can be designated for military service—presumably to be further trained as officers while others can go on for professional training.

This is essentially the system adopted in Great Britain. In discussing its application to our American situation, Sir Hector Hetherington, Vice Chancellor of the University of Glasgow, made some rather pertinent comments (*New York Times*, November 29, 1942):

Plainly, as little as possible ought to be left to the young man or his parents. The assumption is that from the age of 18 he is at the disposal of his government and that it is the government's business to tell him how best he can be employed. Anything else imposes an intolerable strain on the young man's conscience. Hence the selection should be done by a national authority on a basis as objective as possible, such as school records and reports, together with school-leaving examinations and interviews.

Sir Hector's remarks lead us directly into another important aspect of this problem which largely has been ignored in past discussions—that is, the question as to how the young men themselves feel about it.

The normal instinct in man is to fight. In an orderly society functioning along peaceful lines, that instinct is subdued. In time of war, however, we expect to see the fighting spirit manifest itself in every healthy male. We must consequently recognize that many a young man today is asking himself whether he is doing his duty in attending a university or in working in industry while his friends are fighting with the armed forces. The conflict is already going on within him and as we get deeper and deeper into the war along combat lines he will find it more and more difficult to satisfy his conscience. Even though the December 5, 1942, Executive Order prevents his voluntary enlistment, the chances are that he has not become entirely convinced by the decision of his local draft board, a decision which after all was based on a request from his civilian employer. Then there is the pressure of the surroundings-be it real or imaginary. The day may soon come when the vacation trip to his home town will be something that had better be passed up for fear there may be too many questions asked as to why he is not serving his country in uniform. Perhaps there is a dreaded call on the mother of his best friend who was killed in action \* \* \*

Let us be realistic about this and agree that some

January, 1943

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action is called for to clarify the situation. If, at the age of 18, a man is to be placed at the disposal of his government and it becomes the government's business to say in what capacity he can best serve the war effort, then there has to be an official recognition of this fact. We must arrive at some means of unmistakably identifying the man as having been drafted to serve his country in an educational institution or in industry, as the case may be, on a level of duty and performance parallel in importance, if not in danger, to that of the Combat Army.

In his capacity as Chairman of the War Manpower Commission, Mr. McNutt now has the power to define clearly the status of technically trained men under the Selective Service System. Indeed, some phases of the broad problem may have been dealt with before this discussion appears in print. In the meantime, the officers of the AMERICAN CHEMICAL SOCIETY will continue their efforts to arrive at a more satisfactory solution. It is likewise the duty of the individual member to work toward the same end.

As chemists and chemical engineers, we can be proud of our accomplishments so far, and there is no reason to doubt that we shall continue to make good on our obligations in the year which lies ahead of us. We shall feel more certain of success, however, once we have assurance that there will be an adequate and continued supply of technical personnel.

PER K. FROLICH

#### **Detroit Takes Over**

N WARTIME one must become accustomed to rapid change and be prepared to alter plans on short notice. When the Indiana Section invited the AMERI-CAN CHEMICAL SOCIETY to hold the 1943 spring meeting in Indianapolis, no one visualized the conditions that exist now. Late in 1942 it became apparent that the housing situation in Indianapolis was clouded with grave uncertainties. The city is encircled by Fort Benjamin Harrison, Camp Atterbury, Stout Field, and the White River Naval Armory. In September the Government took over certain dormitories at the Indiana State Fairgrounds, Butler University, and Indiana Central College. Hotel facilities were surveyed and it was anticipated that one or more would become Army barracks. At latest report no such action had been taken, possibly because the rooms are filled night after night by travelers who have business with nearby war plants and Army posts.

The Indiana Section realized that it had assumed an obligation and hence did not withdraw the invitation. Without seeing a solution to the housing problem, the section expressed willingness to do everything within its power to take proper care of the registrants. The Board of Directors of the AMERICAN CHEMICAL SOCIETY, however, did not believe it fair to either host or attendants to continue with the meeting plans and suggested postponement. To this the Indiana Section agreed.

When the Detroit Section heard of this decision, it immediately made a survey of the local hotel situation and discovered it to be favorable. Although its every member was extremely busy in essential activities, the section, through its executive committee, voted to invite the Socierry to Detroit because of the firm conviction that the meeting would be an important contribution to the war and few, if any, centrally located cities were in a position to house attendants. The Socierry is aware of the sacrifices that will be made by the Detroit members in planning and operating a national meeting and is deeply appreciative of the attitude shown by them and by the section.

The committee must accomplish in the next few months work usually spread over two years. It will be faced with difficulties in procurement of operating personnel and equipment that were nonexistent in 1940. Fortunately, most of those responsible for that splendid meeting will serve again.

The committee is asking the members of the Society to cooperate in one matter-namely, to utilize hotel rooms to capacity. Although the housing situation is more favorable in Detroit than in most cities, fewer rooms will be available for A. C. S. use than in September 1940. There must be no unassigned beds. In making reservations, please arrange for double occupancy with some friend who will attend the meeting. Do not ask for single rooms. Do not bring to Detroit guests who will not contribute to or gain from the discussion of technical war problems. Give the committee accurate information concerning times of arrival and departure, so that hotel rooms can be assigned with greatest efficiency. Make your reservation through the committee, not the hotel. Such cooperation is easy to give and involves only minor inconveniences when compared with that voluntarily assumed by the Detroit chemists for your benefit.

This will be a War Meeting. There will be no plant trips, no entertainment. Even more than the customary emphasis will be placed on technical sessions and opportunities for conferences and discussions. Group meals and social hours will be encouraged as a means of bringing attendants together.

Everyone planning to attend should arrange for the following as soon as possible:

(1) Hotel accommodations (see *Chemical and Engineering News*, January 10, 1943, for instructions).

(2) Pullman space from your home to Detroit and return.

Difficulty will be avoided if no one makes the trip without prior attention to these two matters.

ALDEN H. EMERY

#### Food à la Guerre

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**FOOD**, probably the original subject of prehistoric man's division of labor, is the focal point of a vast amount of accelerated development now. Nutritional considerations and concentration of maximum food value in minimum bulk and weight are paramount. Balance of vitamin content, preservation of food values under all climatic conditions to the time and place of need, and above all the safeguarding of the robust good health of our fighting men are vital factors in this wartime revolution in the food industry.

Fortunately the elements of the matter are well understood. Their application by the food industry to the problems at hand has been prompt and efficient. New techniques of handling and packaging have been developed rapidly to meet the needs. Elsewhere in this issue a symposium of some seventeen papers deals in considerable detail with these vital matters. Obviously chemistry and chemists were ready to share the burden in this as in other developments necessitated by global war.

#### **Permanent Makeshifts**

EVIDENCE multiplies that many of the makeshifts forced upon industry by the exigencies of war are here to stay. So useful are many substitutions that they will undoubtedly become standard practice even after peace again fosters free flow of traditional materials in international trade. Outstanding among our national shortages are tin, silk, and rubber. These have caused grave concern to the industries needing them, and each has under the force of necessity given way to what were originally considered makeshifts. Already the erstwhile makeshifts are proving so satisfactory that these materials are likely to find many customary markets closed to them at war's end.

Rubber, we now realize, has never been completely satisfactory for many industrial purposes. Oils, air, ozone, steam, and even water itself damage rubber on more or less prolonged contact. Only because rubber has been plentiful and cheap and its fabricators highly enterprising has it held its place in many fields in the past. Today numbers of rubbery synthetics, each adapted to serve some particular purpose, entrench themselves firmly in what once was rubber's unquestioned domain. The success of various synthetic elastomers in electrical insulation, in resisting chemical and solvent attack, in "rubberized" cloth for raincoats and the like, and in gaskets and other like applications is phenomenal.

Silk's hold on its last important market, hosiery, weakens as new techniques in knitting rayon and increased output of synthetic fibers establish themselves in a silkless market. Tinless alloys, plastic collapsible tubes, and even tinless cans by war's end may well reach a state of public acceptance that will remove tin from critical lists.

How far these and other developments may go in changing our views of essential raw materials can be only surmised. Certainly goads to ingenuity in avoiding critical materials are felt on all sides. When, as now, costs are secondary, pioneering can proceed in directions closed under ordinary circumstances. Industrial courage sometimes needs such stimulation to tackle "insoluble" problems. When that is supplied, results are sure.

#### **Compulsory Flameproofing**

I FCITIES and states are unwilling to enact laws which require the flameproofing of draperies, hangings, and decorations in public establishments like restaurants and night clubs, the Federal Government should provide the necessary legislation. In 1912 Sir William Perkin of England addressed the Eighth International Congress of Applied Chemistry in Washington and demonstrated the flameproofing capacity of tin compounds for cottons. Members of the AMERICAN CHEMICAL SOCIETY who attended his lecture may recall that he had an old cotton-flannel garment which was almost worn to shreds but which was still nonflammable though it smouldered very slowly. At that time Perkin announced that the cost of flameproofing was about one cent per square yard.

A professor in one of our large urban universities in his lectures in general chemistry since 1912 has referred to the desirability of producing nonflammable fabrics. In that city, not a single department store has advertised nonflammable materials in all those years.

Nonflammable materials should be employed in the manufacture of children's garments. There is hardly a day during the winter season that some poor child does not suffer from severe burns through contact with fire. The safety of America's children would in itself seem to justify compulsory flameproofing of fabrics.

If permanent fireproofing materials are subject to allocation at present, more publicity should be given to compounds which have been announced recently for rendering materials nonflammable if used in the rinse water in laundering. This at least would let the public know that protection is possible.

How many Boston holocausts and how many horrible deaths of children are necessary to bring about protective legislation?

#### ALEXANDER SILVERMAN

Research is finding out what we are going to do when we can't keep on doing what we're doing now.

CHARLES F. KETTERING

# YEAR OF WAR

**N**ETEEN forty-two began 24 days early. Despite the calendar, December 7, 1941, was the first day of 1942. On that day the United States was jolted suddenly from defense into war. The transition in national thinking occurred in the bursting of a few bombs and was completed almost before their echoes had died away. Although the change of view was complete, the year was well nigh spent before tactics of defense were displaced by advancing offensives by our armed forces. Problems of supply in bulk and continuity over vast distances loomed even larger than those of production. The momentum given production in 1941 carried the efforts to greater heights than had ever been reached before.

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#### Rubber

The synthetic rubber squabble was one of the biggest technical fights ever aired in the newspapers, and only ceased on the appointment and final report of a three-man committee composed of Bernard Baruch, James Conant, and Karl Compton, which studied the synthetic rubber problem and ways to expedite production.

The beginnings of the confusion appeared when Thurman Arnold, Assistant Attorney-General, and the Standard Oil Company of New Jersey tangled in an antitrust action which was settled in March by the signing of a consent decree. This terminated the Standard-I. G. contracts and made available (on a royalty-free basis for the duration of the emergency) some two thousand patents obtained by those contracts. At this point the Senate Committee to Investigate the National Defense Program (Truman Committee) started an investigation into all phases of the rubber shortage. Secretary of Commerce Jones, before this committee and otherwise, defended his record both in accumulating raw rubber in stock piles as head of the Rubber Reserve Corporation, and in encouraging synthetic production as head of the Reconstruction Finance Corporation. Reserves of raw rubber were said to amount to 700,000 tons at the beginning of the year. and synthetic rubber capacity was scheduled at a rate of 40,000 tons per year. There was no great pressure for enlarged synthetic production until Malaya and Singapore surrendered to the Japs. This was followed by the hard-fought campaign to hold the Philippines and the Netherlands East Indies. One of the important results of this series of military defeats was to cut off the supply of raw rubber. Shortly thereafter all civilian nonessential uses of this substance were prohibited or sharply



### INDUSTRIAL AND ENGINEERING CHEMISTRY



curtailed in the United States, and the goal of synthetic production of rubber was raised to 700,000 tons annually.

During the Truman investigation a refugee Pole, Waclaw Szukiewicz, told of producing butadiene, vital raw material for synthetic rubber, out of alcohol which, in turn, was produced from farm products. It was further testified that an investment of \$75,000,000 would produce enough butadiene for a 700,000-ton rubber program. From then on it became anyone's fight. Pressure groups, farm blocs, inventors, oil companies, all clamored to be heard and asked special attention and consideration. Most pressure came from the farm bloc demanding that alcohol from farm products be the genesis of butadiene. The oil companies were just as insistent that petroleum hydrocarbons remain the chief source. While the investigation was underway, the Government instituted a drive for the collection of scrap rubber and designated gasoline filling stations as salvage centers. The response was immediate and well over a year's capacity for reclaiming plants (350,000 tons) was collected before the intensive campaign concluded.

For a while the problem was deadlocked, with War Production Board officials claiming that the alcohol-rubber program would use critical materials ill spared from the war effort. Countering this claim were statements of alcohol experts that this might be true but the alcohol program could get underway faster. The advocates of natural rubber from guayule shrub, rabbit brush, and *Cryptostegia grandiflora* were demanding that stupendous planting programs be started immediately.

Before the Senate Agriculture Committee, Donald Nelson admitted that if he were to start the synthetic rubber program "all over again, I would build a much larger percentage" of plants using alcohol for production of rubber substitutes. He indicated that 25 per cent of the output would be obtained from the alcohol process.

On August 6 President Roosevelt appointed the Baruch Committee to study the whole rubber picture. In the meantime the Truman report had made public the fact that our serious position in rubber was due to careless use of tires by \*

Copper Smelters, Such as This Massive Plant of Anaconda Copper Company, Are Producing at Utmost Capacity to Supply the Demands of War for Metal the Army, an orgy of rubber consumption, the concern of British and Dutch rubber interests, with a possible American monopoly if stock piles were built up, the Standard Oil and German cartel agreement, and a delay in formulating a synthetic rubber program.

Inventions and schemes, good and bad, beset the nation. Materials that felt like rubber were shipped to the National Inventors' Council from all over the United States, new chemical processes were reported for reclaiming rubber, new ways to recap tires were publicized. While the Baruch investigations were un-

derway, much of the commotion ceased. One of the clearest statements on the problem was the report of Elder (2) at the AMERICAN CHEMICAL SOCIETY'S Buffalo convention on the production of butadiene.

The Baruch report provided a complete program when it was made public on September 10. It advocated nationwide gasoline rationing to conserve rubber now on cars, a national speed limit of 35 miles per hour, and appointment of a Rubber Administrator to expedite the program. These suggestions were all followed; William M. Jeffers was appointed administrator and Bradley Dewey, his deputy.

Further, the Baruch Committee revealed that the present plans for the production of synthetic rubber, as outlined by the governmental agencies concerned, call for the erection of certain types of plants in the United States (1). Once the report was made, the agitation ceased and, out of a confused muddle emerged a positive program designed to produce rubber with the least possible delay.

#### Government and Legislation

During February, the Treasury Department seized the German-dominated General Aniline and Film Corporation, placing the stock under the control of Leo T. Crowley, Alien Property Custodian. Over 97 per cent of the stock was transferred in the move. Later Secretary of the Treasury Morgenthau appointed Robert E. McConnell, Robert E. Wilson, George Moffett, and A. E. Marshall as managing directors of the corporation. McConnell is acting as president and is chairman of the four-man board. In further moves the Alien Property Custodian took over control of General Dyestuff Corporation, selling agency for General Aniline.

Large numbers of enemy-owned patents were also seized and made available to responsible companies as a means of speeding up the war effort. In a historic decision even enemyowned patent applications, heretofore held in inviolable secrecy, were opened to American industry. Publication of printed copies of patent applications was to begin in December.

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Government seizure also included the foreign stock of Magnesium Development Corporation of New York, organized jointly by the Aluminum Corporation of America and the I. G. Farbenindustrie. The action of the Alien Property Custodian followed by several months the antitrust proceedings against the corporation as a monopoly. Stemming from this suit was the decision by Magnesium Development Corporation to relinquish its interest in patents involving the manufacture of magnesium.

Assistant Attorney General Arnold was further active in the chemical field when he indicted eight corporations and twenty of their officers on charges of conspiring to monopolize the dyestuff industry throughout the world. The companies were E. I. du Pont de Nemours & Company, Inc., General Aniline & Film Corporation, Allied Chemical & Dye Corporation, American Cyanamid Company, General Dyestuff Corporation, Ciba Company, Inc., Sandoz Chemical Works, Inc., and Geigy Company, Inc. The indictment contained three counts, charging a conspiracy which eliminated competition in the United States, restricted imports and exports, and extracted exorbitant prices from consumers. The trial of the companies has been suspended for the duration of the war, however—a move taken to expedite production of war materials by the indicted firms.

Thurman Arnold also continued his activities in the patent field, seeking to end those abuses of the patent laws which violated the Sherman Act. His views on this subject were often vigorously disputed by industry, and patents became one of the most controversial issues of the year.

The Supreme Court, in a unanimous decision in the case of G. S. Suppinger Company vs. the Morton Salt Company, ruled that a company which uses a patent monopoly to suppress competition in unpatented articles may not obtain legal relief against infringement of the patent. Chief Justice Stone said: "A patent operates to create and grant to the patentee an exclusive right to make, use and vend the partic-

ular device described and claimed in the patent. But a patent affords no immunity for a monopoly not within the grant and the use of it to suppress competition in the sale of an unpatented article may deprive the patentee of the aid of a court of equity to restrain an alleged infringement by one who is a competitor."

Later in the year the court ruled that the holder of a patent could not control the resale price of a patented article by stipulating the price to be maintained by vendors without violation of the Sherman Act. "The Patentee", the Court said, "exhausts his limited privilege when he disposes of the product to the agent. He then has, so far as the Sherman Act is concerned, no greater rights to price maintenance than the owner of an unpatented commodity would have."

The decision of the court handed down in 1941, popularly referred to as the "flash of genius" decision, came in for considerable discussion during the year in the pages of *Chemical and Engineering News*.

In the patent field most technical societies were interested in Paint Coats Are Dried in 8 Minutes by Two Batteries of Infrared Drying Lamps, Six to Eight Times as Fast as the Steam-Vented Ovens Formerly Used— Speedy Production Is America's Answer to the Axis

Westinghouse Photo

Senate Bills S2303 and S2491. The AMERICAN CHEMICAL SOCIETY through its Patent Committee printed analytical summaries of the bills, and urged interested companies and individuals to express their opinions to their senators. The bills were defeated.

#### Labor

In a momentous decision handed down on January 13, 1942, the National Labor Relations Board held that professional employees cannot be forced into a heterogeneous bargaining unit unless a majority of the professional group had indicated by vote that they wished to be included. The decision was given in the case of Shell Development Company and the International Federation of Architects, Engineers, Chemists, and Technicians. The controversy started when the company and union were unable to agree upon the composition of a unit for bargaining purposes for both professional and nonprofessional employees of the Shell company.

#### Man Power

The chemical process industries, like all others in wartime United States, were in 1942 expanding toward new records in production. One of the unwanted by-products of this development was a growing shortage of man power to run and supervise new plants. Principal difficulty seemed to be the inability of employers to get exemptions for necessary and important personnel. The armed forces were taking all comers sent up by local draft boards and making no serious attempt to discourage the induction of technical men. Most employers soon learned that it was necessary to appeal local draft decisions to state and even national authorities, and this procedure was successful in keeping men where they could use their training to the fullest extent in industry.

The need of men by the Army could not be denied, but



serious doubts were cast on the desirability of mobilizing 10,000,000 men into the service. Toward the end of the year it seemed certain that a reduction in the ultimate number of men in all branches of the fighting forces might be necessary to balance production and fighting services.

The fight to keep chemists and chemical engineers out of the the Army and in industry was led by the AMERICAN CHEMICAL Society, and *Chemical and Engineering News* continuously carried latest information on the subject. Critical shortages of trained men were predicted as the huge programs of highoctane gas, synthetic rubber, and light metals were piled on top of the already magnified chemical production.

Chief point, aside from the crucial necessity of keeping production running with able men, was the fact that 27,000,000 men were available to Selective Service in the draft group (not including the 18-19 year old group which was scheduled for registration late in the year) as against only 250,000 trained scientists and engineers upon whom the success of the whole technical program depends.

Trained men could be kept in the production army where they belonged, instead of the combat army where their talents might be largely wasted, only if the proper procedures were taken. In addition to educating the local Selective Service Boards to the needs of industry, there was the necessity of convincing both the employer and the employee that it was both patriotic and proper for an effort to be made for the retention of specialized personnel.

#### Shortages

Material shortages continued to pile up. To those living on the eastern seaboard the activities of the German U-boat pack brought home a shortage of two items—gasoline and oil. Early in the year this area was put on a strict gasoline rationing of 3 gallons per car per week. Though later this was increased to 4 gallons, the invasion of North Africa by American forces created such a drain on tanker service that the ration

was again reduced to the 3-gallon basis for nonessential driving. Fuel oil rationing for similar reasons had the residents of these zones thoroughly puzzled and worried about the source of their winter warmth. Original plans called for maintenance of a 65° F. temperature throughout the home, but this appeared likely to be reduced to 60° as the year came to an end without any solution to the problem of adequate supplies of oil to the eastern area.

In the industrial field the year started with shortages of fifty-odd items, according to the Bureau of Industrial Conservation of WPB. As materials were consumed in ever-increasing amounts, these items were joined by others. The October releases of the same bureau listed over one hundred metals, chemical, and miscellaneous products, the supply of which was not sufficient for war and essential civilian uses. Consequently they were entirely prohibited for civilian use. In this respect the chemicals juggled positions. Thus, formaldehyde began the year in

Tons of Iron and Steel Turnings, By-Products in the Manufacture of War Implements, Are Returned to the Production Line in the Form of Two-Pound Circular Bricks That Roll Off a Newly Installed Briquetting Press at the Rate <sup>3</sup> f 1000 an Hou

Westinghouse Phot

group I, the select group of not enough for war uses. Before long it had dropped to group II, a tight supply but with some available for substitution of more critical items. Ammonia and its products climbed all the way from groups III and II to group I by the end of the year and supplies were extremely tight.

**Even** in group I there was an even more select section of chemicals considered most critical. Among these were acrylonitrile, butadiene, cresols, phenols, toluene. Styrene did not appear in any of the lists, but its entrance was expected among most critical substances as the tremendous production for Buna S got underway.

In metals, aluminum, copper and its alloys, magnesium, molybdenum, nickel and its alloys, tantalum, tin, tungsten, tungsten carbide, and vanadium were extremely critical. Other raw materials critically short were copra, cotton linters, Manila fiber, coconut and tung oils, all rubbers, shellac, and silk.

Titanium pigments dropped from group I to group III in the course of the year, while iridium made the trip in the opposite direction. Changes like these were to be expected as production plants swung into operation and civilian uses were curtailed.

New sources of metal were eagerly sought and developed. A big new vanadium find in western United States and in Ontario, Canada, was hinted in the press but substantiation is still lacking. The United States Bureau of Mines announced a new explosion shattering machine which would greatly aid in increasing manganese production. It was to be tried out on the shale deposits of low concentration manganese located in South Dakota.

The vast aluminum and magnesium productions planned for 1942 were well underway and turning out quantities of metals that the Axis plus its subjugated lands could not match. A \$350,000 pilot plant for the production of zinc by a gas-reduction process was planned by the Bureau of Mines during the past year. This move is thought to pave the way



January, 1943

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Square - Braided Packing, Made from Continuous Filament Rayon "Tow", Is Serving War Industry in Water Pumps, Accumulators of Hydraulic Presses, Punches, Etc., Where It Replaces Packing Made of Imported Long-Line Flax

> Courtesy, Du Pont Company

sium production at the great new plant of Basic Magnesium Inc. This is the world's largest magnesium plant, and capacity was said to be three and a half times the total 1941 magnesium production. Full capacity of the plant is to be reached about April, 1943.

General Electric Company built a plant for the synthetic production of phenol in Massachusetts. It was to have cost over \$1,000,000 and production was scheduled to start in September at a rate equal to about 75 per cent of G. E. requirements.

Monsanto Chemical Company opened a new plant in Michigan which, in the main, will be devoted to industrial chemicals derived from phosphorus. The plant is established on a 138-acre tract.

The Standard Oil Company (Indiana) was awarded a government contract to build a toluene plant. This is reported to have a capacity equal to the total annual output of toluene in the United States during World War I.

> New Developments Due to Shortages

The shortages brought out the American engineers' habit of substitution and invention. Thus, the United States Mint began experiments, which failed, on glass one-cent pieces in an effort to save copper. Plastics were also considered for the same purpose. Five-cent pieces with no nickel content made their appearance, their composition being 56 per cent copper-35 silver-9 manganese.

The rubber shortage caused adoption of available substitutes for many industrial operations. WPB in an effort to conserve rubber for the armed forces, prohibited rubber's use for many machines and products necessary for continuance of the war effort. Industry was forced to find alternates, and high priorities enabled the acquisition of many new, and sometimes old, untried substitutes. Thus polyvinyl alcohol was used by Radio Corporation of America to replace rubber in hoses, flexible guards, sheeting, and other applications.

Vibration insulation for heavy machines was once again being made from felt, long battled by rubber composition insulation for this market. Raincoats for the Army were made from Saflex resin, Monsanto Chemical Company's polyvinyl composition. In this use they save more than 1.75 pounds of rubber and at the same time make a coat that is some 2 pounds lighter than the conventional type.

In most cases the new materials that were adopted to take the place of the unavailable regular products held promise of never again relinquishing their new found places. Thus Saran tubing, Dow's tubing of vinylidene chloride, was being used to replace copper tubing in refrigeration units and was found to be quite superior to that metal. Melamine plastic buttons, used now chiefly in army uniforms, are certain to hold postwar markets over the vegetable ivory or pearl product formerly used. New resins incorporated in paper pulp while still in the beater will be important in civilian life, after its present use for the armed forces in producing superior crease-resistant blueprint stock and high wet-strength wrapping paper is over. Tubes for tooth paste, shaving cream,

for development of large untouched reserves of domestic ninc ores. The pilot plant located in the south central section of the United States will have a daily output of 500 pounds of metallic zinc. Representing a departure in metallurgical process for treatment of zinc-bearing ores, the bureau's method uses reducing gas in several stages of a reducing cycle from which zinc is obtained in high concentration. Experiments indicate that only 5 cubic feet of reducing gas are necessary to produce 1 pound of zinc and that as much as 95 per cent of the zinc can be extracted from the ore by the new process.

Production of aluminum from low-grade domestic bauxite and clay was recommended to the WPB by the Advisory Committee on Metals and Minerals of the National Academy of Sciences. Use of a proposed new process by the alumina plants in the country will make it possible to include a substantial quantity of clay with the bauxite feed, so that less bauxite will be needed and the limited domestic reserves conserved. The committee has found that treatment of the tailings from the Bayer process (containing iron, titanium, and silicon compounds) by a recently developed sintering process will recover substantial amounts of alumina. Later news from the Department of the Interior stated that engineers and geologists from the Bureau of Mines had blocked out more than 500,000 tons of valuable bauxite in two Georgia counties. Submarine activity on the east coast having slowed up delivery of bauxite from South America, it became feasible to investigate the domestic deposits. Some of the bauxite uncovered could be used immediately. It was indicated that out of 500,000 tons uncovered, over 200,000 tons contained better than 50 per cent alumina.

Sponge iron as a substitute for iron scrap in steel furnaces was much in the news. A commercial size plant was under construction in Wyoming as a Bureau of Mines project. This location was chosen because of its nearness to available sources of iron ore, natural gas, and coal.

Late in the year WPB announced the beginning of magne-





A Bale of Bubblfil, So Light That the Lady Can Easily Hold It, Is Designed as a Replacement for Kapok in Life Jackets and Rafts and for Sponge Rubber as a Shock Absorber

> Courtesy, Du Pont Company

that could be put up in cans and by limiting the weights or thickness of tin plate on the steel base. The capacity of an American smelter being built in Texas has been greatly increased since the war began. This plant will use Bolivian ores.

The lack of tin caused can manufacturers to develop new methods of fabrication. American Can Company announced the perfection of a method for making containers with fiber bodies on machines used for the manufacture of the conventional metal containers. Macmillan Petroleum Corporation also came out with an all-fiber can with a plastic liner.

Plastics were important in detouring scarcities. Thus plywood planes, only possible because of the superior qualities of the resin adhesives used, were being made in quantities as trainer planes. This relieved the direct pressure on aluminum and steel ordinarily used in these ships. The Fairchild AT-13, ordered to mass production by the Army, is made almost entirely from plywood except for steel in engine mounts and

cowlings, and tubular steel members for the support of bomb racks, machine guns, etc. Monsanto Chemical Company announced a new transparent plastic window pane laminated with wire mesh, which would stand the explosion of a 150pound bomb 8 feet away.

Cellophane for candy bars was another war casualty as WPB, in an effort to save this material for war packaging, prohibited its use for confectionery purposes. It was estimated to save some 50,000 tons of wood pulp, and huge amounts of sulfuric acid, chlorine, glycerol, and caustic soda.

The Japanese occupation of Java cut us off from supplies of kapok, necessary as filling for life belts and preservers. The chemical industry devised two solutions to the shortage. Du Pont brought out Bubblfil, a hollow viscose thread with large bubbles of air entrained at definite intervals. The trapped air bubbles made the material extremely light (1.5 pounds per cubic foot), and 3 pounds of this material are sufficient to keep a man's shoulders out of the water. This product was made in large quantities at a Tennessee plant; it is used in life jackets and rafts, to replace sponge rubber in seats and mattresses, and as heat insulation in flying jackets and sleeping bags.

Pittsburgh Corning Corporation also put gas to work in making glass that would float. This, too, was designed for use with various devices for lifesaving in the Navy and Air Corps. The new material, Foamglas, weighs 10 pounds per cubic foot and can be sawed, drilled, and worked in an ordinary manner. Last year, under a certificate of necessity, a large factory was built for the production of the material.

Synthetic sapphires and especially hard glasses were also made by American companies as a replacement for jewel sapphire bearings cut off by the war and important in the construction of delicate precision instruments.

The Northern Regional Research Laboratory of the Department of Agriculture, at Peoria, Ill., developed a synthetic polymer from soybean and corn oils to replace rubber. Called "Norepol", this material is said to stretch 200 per cent or more and return to the original shape. Tensile strengths are approximately 500 pounds per square inch.

and lotions could not be made from tin or lead sheets, so tubes of cellulose acetate, introduced for the emergency, will undoubtedly hold a permanent place in our economy.

1942 may have been a year of unparalleled shortages, but it also was a year of unparalleled ingenuity on the part of the chemical world. The need expressed in the Baruch report for a national production of 60,000 tons per year of polysulfidetype synthetic rubber provided one branch of the chemical industry with an opportunity of demonstrating its adaptability. The Ethyl Corporation had in stand-by condition two plants formerly used to make ethyl chloride by the Frei process using alcohol and hydrochloric acid. These had been supplanted by the more efficient and cheaper process of chlorinating petroleum gases to obtain the same results, and two modern plants were built and running, based on this technique. The pressing need for ethylene dichloride for use in making the polysulfide-type material caused the Ethyl Corporation to return to the older alcohol method and plants for their supply of ethyl chloride; the two new plants were then converted over to make necessary ethylene dichloride by using ethylene from petroleum gases and chloride. No letup in Ethyl fuel production could be allowed by the change, for the fighting forces were taking about two thirds of Ethyl's production, and the other third was going to civilian uses, already strictly rationed. In such a manner were the vital needs of America being met, for the Ethyl Corporation, already producing a vital war material, tetraethyllead, swung over into a new field to manufacture another vital substance.

Recovery of tin from used cans became a war necessity because normal imports of tin were cut off by the military success of Japan in the Far East. Ordinarily uneconomic, war necessity has made salvage of tin from collected cans a "must". Metal & Thermit Corporation announced a new alkali process for detinning cans; they stated that a pilot plant, operating for the past five years in the San Francisco area, had been signally successful. The pilot plant is a complete unit with a capacity of over 6000 tons annually.

Added to the saving of tin through recovery, WPB acted to conserve stocks of this metal by drastically limiting the foods i

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#### Foods

Dehydration of foodstuffs reached national importance. By removing water from food, considerable space is saved in shipments to our armies and Allies, and another but less pressing reason for dehydration was found in the action of the Government in preventing the use of tin cans for certain civilian foods. By removing the water from these products, manufacturers could supply them in paper or other containers not under restriction. A third factor which made dehydration a necessity was the lack of refrigerated transportation and facilities both for shipment of food and for storage at the battlefield.

A shortage of fats and oils loomed for the United States. Cut off from their normally imported oils from the Far East, ways were being sought to make up an estimated deficiency of some 500,000,000 pounds. Missions were sent to the South American countries to expedite collection of natural oils and fats there. The housewives of the nation were urged to save all the fats and grease normally discarded from the kitchen. WPB officials estimated that over 2 billion pounds of grease were thrown away by the nation's cooks, and an extensive drive to salvage a fourth of this amount was started. Posters and radio appealed to the women to save all their fats and to sell them to the neighborhood butcher. Principal reason for this was the need for glycerol for explosives. Nitroglycerin is used admixed with nitrocellulose and alone in certain military applications.

Exploded during the year by a quartet of physicians was the notion that gelatin had superior qualities in reducing fatigue and increasing the energy of workers.

The newly formed Nutrition Foundation pushed its funds close to the million dollar mark and founded a monthly journal, *Nutrition Reviews*. The foundation has thirty-six



Paint Brushes with Natural Bristle (left) and with Tapered Nylon Bristle (right) after Being Used for the Same Length of Time, Tapered Nylon Wears at Least Three Times Longer Than Natural Bristle

> Courtesy, Du Pont Company

supporting members, and its purpose is to further research in nutrition.

#### Medicine

On the medical front most important news was the phenomenal record hung up by the sulfa drugs in the prevention of infection in military casualties. First imposing success was with the British at and after Dunkirk. American military medical men had their first experience of sulfa drugs in largescale use during the Pearl Harbor attack. By dusting the powdered drug into the wound, tetanus and gas gangrene are effectively stopped and the results of the treatment far surpass even the most optimistic expectations. Important too was the announcement that large scale tests by the United States Public Service had confirmed the previously known fact that sulfathiazole was a specific against gonorrhea. Importance of this announcement lay in the speed of cure, said to be five days for 80 per cent of the cases tested.

Discovery of the structure of biotin was announced late in the year by Vincent de Vigneaud at a meeting of the New York Section of the AMERICAN CHEMICAL SOCIETY. This discovery is expected to pave the way for the synthesis of this vitamin. At present there is only 0.1 ounce in the world. The empirical formula of biotin was established about two years ago at Cornell University Medical College. It is now known to be 2-keto-3,4-imidazolido-2-tetrahydrothiophene*n*-valeric acid.

A new material, hemostatic globulin, which will successfully prevent excessive bleeding from wounds was developed by Lederle Laboratories, Inc. This material is especially important to hemophiliacs as it ensures them against dangerous hemorrhages after minor surgical and dental care. Hemostatic globulin supplies prothrombin to the bleeding capil-

laries and causes clotting. The material was first isolated by I. A. Parfentjev from clear blood plasma.

Japanese conquests cut us off from the chief sources of our supply of quinine which, with rubber, was formerly a native of the western hemisphere. Ardent searches for antimalarials, both synthetic and natural, held promise of success and of permanently freeing the United States from foreign domination in this field. A. C. S. President Harry Holmes instituted a campaign late in the year to collect unused quinine from chemical laboratories for use in the medical field.

Sulfadiazine found new usefulness in the treatment of burns. Used in ointments and as a solution, cures were effected in burned skin areas in a fraction of the time normally required by conventional methods and, more important, the burned area heals without scarring. This new treatment is effective even in thirddegree burns and holds promise of enabling more effective control to be exercised in rehabilitating badly burned individuals.

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# PRESERVATION OF

## Food requirements for overseas use

CAPTAIN VIRGIL O. WODICKA Q. M. C. Subsistence Research Laboratory, Chicago, Ill.

• • The Quartermaster Corps Subsistence Research Laboratory is a technical liaison agency between the Army and the industrial and academic institutions dealing with foods. Its chief function is to bring the food requirements of the Army to the attention of a proper development agency so that suitable products can be evolved, and to study production and packaging in the food field so that immediate use of the most recent developments can be made by the Army. It is also responsible for formulating combat rations and exercising technical supervision over their production.

In order to prepare menus for combat rations and to draw up specifications for items of nonperishable subsistence, it is necessary that the laboratory have as much information as possible on all items which might be considered for this use. The laboratory needs available information on foods which can withstand storage at 100°F. for a year without undue development of rancidity or serious loss of flavor or vitamin content. Such foods must be as high as possible, not only in calories per 100 grams, but also in calories per cubic inch.

The laboratory is in urgent need of concrete experimental data on stable, concentrated, nutritious, and palatable foods which are now in existence as well as on those which can be produced from available raw materials with a minimum of modification of existing production equipment.

TN CONSIDERING the food requirements of our Army for overseas use, it is probably well to review first the existing ration structure into which the foods are fitted. The U.S. Army ration is officially the food allowed for one man for one day. In this country and, in so far as practicable, overseas as well, the basic ration for our troops is Field Ration A. This designation covers more the method of procurement and issue than the foods involved, since Field Ration A is composed of just those foods, perishable and nonperishable, which you and I eat every day. Master menus are made up well in advance for each month by the Office of The Quartermaster General and submitted to each service command (formerly called "corps area") in this country. Since the commanding general of each service command is charged with responsibility for the nutrition of the men in his command. these menus are suggestions only, but in practice they are followed rather closely because they are based on expert

knowledge of what foods will be available in the various producing areas during the period covered and are checked over for nutritional quality by specialists before release. Where the local situation indicates the desirability of change, the commanding general of the service command or the commanding officer of the post using the menu may make the necessary changes before the food is purchased and shipped. The menu on which the food is actually issued is then sent to the Office of The Quartermaster General for a final check of nutritional quality and file.

Actual food purchase is made on the basis of these final menus. Perishable items are procured by Quartermaster Corps market centers located in important food centers of the country. Nonperishable items are procured by strategically located Quartermaster depots. By thus centralizing procurement, the Army gains all the advantages of mass buying and proper procurement planning.

Troops overseas also subsist, in so far as possible, on Field Ration A. Menu planning and procurement are handled by Quartermaster Corps specialists on the staff of the commanding general of the field forces concerned. In regions of restricted food supply, however, where food must be supplied from this country, refrigerated transportation is not available to allow supply of all the perishable food items required, and the men must be shifted to Field Ration B.

The B ration is composed entirely of nonperishables—that is, such staples as sugar, flour, salt, etc., and canned or dehydrated meats, fruits, and vegetables. Menus for the B ration are also made up by nutritionists in the Office of The Quartermaster General to suit the climatic conditions in which the troops are operating. Supply to the field forces is made on the basis of these menus unless the commanding general of the force involved directs that changes be made to suit local conditions. Partially because of the restricted variety of properly preserved foods, and partially to simplify the problems of procurement, transportation, storage, and issue, the menus repeat themselves on a ten-day cycle. The cycle is deliberately more than one week and less than two weeks to avoid the association of certain menus with certain days of the week. Such an association has been found in the past to give rise to complaints of monotony which are much less common on the ten-day cycle.

The rations so far discussed are those on which our troops are subsisting in garrison, both at home and overseas. The rations to be described subsequently are operational rations, all of which have been developed in the Subsistence Research Laboratory.

Presented before the Division of Agricultural and Food Chemistry at the 104th

# FOODSTUFFS

#### Subsistence Research Laboratory

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In the fall of 1920 the need for a training center for subsistence personnel led to the establishment of a Quartermaster Corps Subsistence School at the Chicago Quartermaster Depot. The school was opened with a staff of three and a a class of two. In January, 1921, the school was firmly enough established to take in a class of sixteen for an elevenmonth course. In the years that followed, the school continued to operate on essentially the same scale, although the staff was increased to five. Within the limitations of time and funds available, a certain amount of research work was carried on during this period, although the primary function continued to be that of instruction, including the writing of the textbooks used. Many of the current key officers in subsistence work, from General Hardigg down, studied at the school during this period. The last full class was graduated in May, 1936, and immediately thereafter the school was redesignated "Subsistence Research Laboratory". While several small classes have undergone instruction since this time, the courses have been shortened, and the primary emphasis has been on research.

The laboratory continued through late in 1940 with a staff never numbering more than five men, but at that time the pressure of development work combined with a somewhat greater availability of funds started an expansion which accelerated as the war became more imminent until today, when the staff numbers sixteen officers, four civilian technicians, and clerical help.

The laboratory regards its primary function as that of liaison between the Army on one hand and the universities and food industries on the other. Almost all the members of



Photo by U. S. Army Signal Corps

Contents of the Supper Unit of Field Ration K

Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y.

Vol. 35, No. 1

the staff have both military and technical backgrounds to aid in carrying out this purpose. The technical problems involved in developing foods for army use are so many, so varied, and so great that no one agency could hope to undertake their solution unaided. Conversely, even though food technology in this country may be the most advanced in the world, no efficient use of it can be made by our Army without an agency which can speak and understand both military and scientific language; military needs must be translated into concrete projects for the food industries and technical institutes, and the military usefulness of new developments in food science and technology must be recognized. The Subsistence Research Laboratory carries on no research projects which other agencies are able and willing to undertake, but tries chiefly to correlate the research being done and to adapt it to military use.

> Field Ration K Is Stable and Palatable under Conditions of Arctic Cold or Desert Heat Photo by U. S. Army Signal Corps



Specific mention should be made of Ancel Keys and his group at the University of Minnesota. Because of the unusual facilities existing there, invaluable work has been done in testing out combat rations under various conditions of climate and performance. Lately the Harvard Fatigue Laboratory, with similar facilities, has undertaken some of this work in addition to its earlier studies of clothing and equipment and has already contributed materially in this field.

#### **Operational rations**

The chief operational ration now in use for tactical situations in which the field kitchen cannot be used is Field Ration C. One C ration consists of six cans. Three of them, one for each meal, are identical; each contains special biscuits, hard candy, soluble coffee, and sugar. The other



three cans, also one for each meal, are different. One contains meat and beans, one meat and vegetable stew, and the third meat and vegetable hash. All three of these products, as well as the biscuits in the other cans, are special items having no counterpart in previous or current civilian production. The ration can be eaten cold, although it is more palatable if the meat units and the coffee can be heated. Work on the C ration started in 1935, and the initial pilot procurement was early in 1940. Although it is a material improvement on the earlier iron rations of hardtack, corned beef, beans, and chocolate, we at the laboratory consider it

somewhat obsolescent in the light of later developments.

The ultimate emergency ration is Field Ration D. This consists of three 4-ounce chocolate bars, specially compounded so that they will not soften unduly at even desert or tropical temperatures, and reinforced with thiamine chloride to help metabolize their calories. This is also a special product with no commercial counterpart. It was developed by Colonel Logan in 1935 during his tenure as Assistant Commandant of The Quartermaster Subsistence School.

The remaining combat ration is Field Ration K. Development work started early in 1941, and the first production for other than test purposes was begun in July, 1942. Work was begun in response to a request from the parachute troops for an extremely light and compact ration to be carried on their jumps. It has proved so satisfactory that it bids fair to replace the C ration for all combat 80

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use. The ration consists of three separate units, one for each meal. Each is packaged in a moisture-vapor-resistant, gasresistant, nonmetallic container, and contains two different types of biscuits, canned meat or cheese, a confection, a beverage concentrate, chewing gum to allay thirst, and four cigarets. The meat units, confections, and beverages are different for each of the three meals.

While this ration has seemed unnecessarily complex to some, the variety contained in it is deliberate. No simpler ration has yet been found which did not become so tiresome within a few days that the test subjects did not eat sufficient to meet their nutritional requirements. On all the tests of the K ration, men who have lived on it for a week have almost invariably indicated their willingness to remain on the ration for as long again, and many have said that they could stay on it indefinitely. Measurements of food intake and objective measurements of performance ability, both in the laboratory and in the field, have indicated that the ration is well tolerated and that the fighting efficiency of the men is maintained.

These, then, are the rations now in use by the Army. Others are in various stages of development, but any discussion of them now would be premature.

#### Guiding principles for designing a ration

The first principle is palatability. No space or weight is saved, and no nutritional purpose is served by bringing to the soldier food he will not eat. The food must be palatable, not only at first but also after frequent repetition.

The second requisite is nutritional value. Each ration must be nutritionally adequate for its specific purpose. This will be governed partly by the length of time the soldier will use it and partly by the duties he will have to perform. Each ration component must contribute its share.

The third indispensable is stability. Most army rations will encounter severe conditions of transportation and storage which will render inedible a high proportion of the foods to which we are normally accustomed.

The fourth basic principle is concentration. All foods for overseas use, especially those which must be transported into the combat zone, must be reduced to the minimum compatible with the other requirements just mentioned in both weight and bulk. Subsistence officers are speaking not only of calories per ounce, but also of calories per cubic inch.

Other factors, such as ease of preparation in the field,

availability, presumptive production capacity, cost, and physiological effect, must be taken into account, but the four basic criteria must be met before any food material can be seriously considered.

Much has been done by the Subsistence Research Laboratory to meet the peculiar problems posed in feeding an army in the field. Even more has been done by private agencies at the instance of the laboratory or with some guidance from it. It is now pertinent to list some of the developments which must be made.

#### Problems to be solved

In general, the laboratory is interested in seeing any foods which meet the basic requirements listed above. None of the rations is immutably fixed, and specifications are frequently revised in the light of later knowledge. If anyone has a food product which has not been submitted to the laboratory and which is palatable, nutritious, concentrated, and stable for a year at 120° F., we want to see it.

More specifically, the laboratory wants to see more foods which are concentrated, stable sources of vitamin C. For various reasons we shun vitamin pills for routine administration. We want our nutrients in foods. We are willing to consider fortification, however, if the resultant product is a stable vitamin source.

Another specific problem is dessert. Desserts are usually rich in calories and are well received by the men. Our list of usable desserts, however, is badly in need of expansion. The products sought must be high in caloric density (calories per cubic inch), must require no preparation, or must be easily prepared by small groups with no cooking equipment and will preferably not be packed in tin.

Along more fundamental lines, we need to know more about flavor. Frequently the only criterion of quality of a product is its flavor, and the state of our knowledge leaves this entirely too subjective a measure to be reliable for specification and control of quality.

Another general requirement is for information. The pressure of work at the laboratory is far too great to allow any of us to do a systematic job of keeping up with the literature. It will help immeasurably if those working on human nutrition, food, or food analysis will mail us reprints of their publications. We cannot otherwise hope to see more than a few of them.

A Typical Dock Scene as Goods in Mounting Volume Arrive at Kansas City Quartermaster Depot

## Food packaging for overseas use

#### CAPTAIN ROBERT R. MELSON

Quartermasters Subsistence Research Laboratory, Chicago, Ill.

is moldy, dry, hard, tainted, infested with weevils, or con-

taminated with a war gas cannot be used to maximum efficiency. The constant thought of this laboratory is that,

no matter how great the calorific value or how adequate the

vitamin content of the food may be, it will not benefit the

soldier if he fails to eat it. If food is allowed to spoil, not

only do we lose valuable material that has been transported

in precious ship bottoms, but there is a possibility of losing

the troops for which it was intended and, subsequently, strategic positions. It is absolutely essential that the Army's

Extreme conditions are certain to be encountered. The

food the Army Quartermaster Corps buys must be packaged

to withstand the rigors of both arctic and tropical climates.

It is impossible to determine whether a shipment of food, on

its way to a port of embarkation, is going to be sent north or

south, or shifted from one to the other after initial shipment. It depends upon what the situation at the moment dictates.

Therefore, packaging materials must withstand temperatures

for  $-20^{\circ}$  to  $+120^{\circ}$  F. or higher, and the humidities may

range from the high humidities of the tropics to the lower

humidities of dry climates. Protection must be provided

against moisture vapor, water, odor transfer, grease transfer, insect infestation, and rats. Due to the nature of the Army's

assignment, only the poorest docks and warehouses can be

expected. Much unloading is carried out under cover of

darkness, possibly in the surf, and supplies may be left on a

beach from one night to the next, exposed to tropical rains.

Often no warehousing will be available. Cases of food may

be loaded and unloaded several times on their long journey

and handling under battle conditions is anything but

food be properly packaged. Many lives depend on it.

• • The Quartermaster Corps is called upon to ship hygroscopic food products, such as dehydrated fruits and vegetables, dry milk solids, and powdered eggs, to both arctic and tropical areas. The problem of packaging for these extremes of climate became critical when war conditions reduced the availability of rubber, tin, aluminum, and steel plate. At present cellophane, waxes, and some enamels are approaching the critical list.

The trend is away from metal and toward flexible packaging materials. Samples of films submitted to the Subsistence Research Laboratory are subjected to vapometer cup tests, and acceptable films are further tested by application to particular products. Resistance to insect infestation, grease transfer, and odor transfer are of interest.

Substantial shipping cases are required, since mechanical abuse is expected and the cartons may be exposed to rain or wet ground. An effort has been made to package the Army's food in toxic war gas-resistant materials. Many materials of varying degrees of resistance have been tested. Proteins, regenerated cellulose, and polyvinyl alcohol give

good resistance; asphalt and waxes, considerably less protection. Chemical decontamination of gassed food stores is difficult.

ACKAGING for overseas use does not arouse a very vivid picture in most minds. We usually visualize some food in large export boxes, sitting on a dock, and then forget it. Actually, packaging is of vital importance, especially to the Army. No matter how high the quality or how great the quantity of the food we buy, it will be useless if not delivered to the troops in edible condition. Food that



Assembly Line for Army Field Ration K

gentle. In spite of these difficulties, we require that food shall keep well for at least a year.

To accomplish this important task, the Army employs all of the major types of packaging. The Quartermaster Corps has specifications for metal cans, fiber cans, drums, bags, sacks, folding cartons, glass containers, kegs, and special packages.

#### Types of packaging

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Metal cans are familiar to all. In peacetimes tinned cans were normally used. These cans were manufactured of plate carrying 1.5 pounds of tin per base box. Over two years ago the possibility of a tin shortage was foreseen, and a tin replacement program undertaken. The weights of all tin coatings have now been reduced. Electrolytic tin plate is available today. This plate carries about 0.5 pound of tin per base box, but affords greater protection than is indicated by this amount because of the method of uniform application. Enamels and lacquers are also used to increase the protection afforded the product by this plate. For overseas shipment, electrolytic plate must be enameled on the outside to protect it from corrosion.

Bonderized plate is also available, and production is being rapidly increased. This is similar to the base plate of the tin can but has been chemically treated to reduce the rate of corrosion. The use of this plate is limited, but as more satisfactory enamels are produced, its application will be broadened.

Deoxidized steel, enameled on both sides, may also be employed in cans. However, its use for overseas shipment is restricted to steel drums, ends of fiber cans, or packing dry products that will be subjected to less severe conditions.

At present electrolytic plate and Bonderized plate are authorized for packing certain dehydrated vegetables and for ends of fiber cans. Electrolytic plate may be used for certain canned vegetables and for the biscuit unit of the C ration.

There has been a general shift downward in the products packed in metal cans. Products formerly packed in heavily tinned cans are now put up in plate carrying a lesser amount of tin or in electrolytic plate. Products formerly requiring a lightly tinned can are now packed in Bonderized or deoxidized steel plate. In other words we are adapting to each product the lowest grade plate that will do the job.

Fiber cans with untinned metal ends are specified for a number of dry products that were formerly packed in tin. The specifications prescribe a can of special construction. the body consisting of a lamination of moisture-vapor-resistant films employing asphalt and wax. This results in a fiber can of much greater moisture-vapor-protective properties than any manufactured before the war. The liners are varied, depending upon the product to be packed.

Enameled steel drums are utilized to replace tin in packing dehydrated fruits and vegetables. However, they are used rather sparingly at the present time since they require a little more metal and space than some other types of packaging.

Cotton sheeting bags inside of five-ply multiwall paper bags are employed to pack coffee, sugar salt, and vegetable



Frozen Boneless Beef in Cartons for Overseas Shipment Compared to Carcass Beef

seeds such as beans, peas, and rice. These products require less protection and are given less protection.

Folding cartons are specified as part of the packaging for such products as cereals, cornstarch, baking soda, salt, and sugar. Inner liners or wraps are usually employed. Our D and K rations come in this category.

Glass jars and bottles are specified for flavorings, extracts, vinegar, and a few other products. However, handling is so rough in the Army that they must be well packed to prevent breakage. We specify as little glass as possible. Recently vinegar was removed from glass, and a search is now under way to replace glass further. Kegs are used for vinegar and some citrus concentrates. They are strong and tight, but are inconvenient as dispensers and rather wasteful of shipping space.

Most of the packages mentioned have been adapted from their peacetime assignments. The chief problem has been in developing special linings and closures so that a given package will carry a more difficult product than normal. However, to pack satisfactorily one class of food which has recently come to the foreground requires a large amount of plate or other critical materials.

#### **Dehydrated** foods

An unusually large amount of dehydrated food products are being utilized for feeding the troops. These foods answer the Army's requirements admirably in reducing weight and volume and increasing storage life. They have an average relative humidity of about 30 per cent at room temperature, whereas humidities above 90 per cent are common in the tropics. Therefore, these products require considerable protection against moisture vapor as well as other outside influences.

With tin plate, black plate, rubber, aluminum foil, and other materials restricted, and waxes, cellophane, and some lacquers nearing the critical list, only more or less elementary

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materials remain for packaging. Our assignment has been fairly well defined. The Quartermaster Corps has the most hygroscopic foods in history to preserve for a year or more under the worst conditions imaginable, with a majority of the good packaging materials restricted from use. In most cases we are trying to duplicate with flexible packaging films the protection originally afforded by tin plate. Although we emphasize moisture-vapor protection, there are other requirements of a packaging film. As previously stated, we expect a packaging material to afford protection against the transfer of odors, grease, and water and to prevent infestation and contamination. However, these latter problems lend themselves to an easier solution than the moisture-vapor question.

When we were confronted with packaging dehydrated vegetables in the less critical materials, it was necessary to choose types of packages and packaging materials for the particular product in mind. In searching for a suitable packaging film, you have a number of basic sheets from which to choose. Glassine, Pliofilm, cellophane, and other cellulose derivatives, sulfite paper, kraft paper, parchment paper, etc., are available. Since many of these sheets offer little protection alone, they are usually coated with a film to enhance their moisture-vapor-resistant properties. Wax was one of the first materials employed in this manner. Now we have numerous modified waxes, nitrocellulose coatings, resins, varnishes, lacquers, and other materials.

It followed logically to combine two of these sheets to obtain additional moisture-vapor resistance. Sheets thus combined into a single film are called "laminated" films. These laminated films were often again coated to improve their properties further. This gives an insight into the enormous number of possible combinations available, expecially when the range of adhesives and plasticizing agents that modern chemistry offers is considered.

#### **Tests on films**

A year or so before the war began, this laboratory began an investigation of these films. Recognizing the strategic character of metals in war time, efforts were concentrated on flexible packaging materials. The laboratory was flooded with a deluge of samples of every composition and grade. It became impossible to test all these materials as prepared packages. A standard method of culling out the inferior sheets was badly needed.

In choosing a method of determining the moisture-vapor transfer rate of films, it was found that no standard equipment was available. Most companies had devised their own method of testing, and each varied from the other in several details. One of the recognized methods was that described by the Technical Association of the Pulp and Paper Industry. However, to be effective, a number of identical pieces of apparatus were desirable, and they were not available. Further search brought to light the testing equipment developed by General Foods Corporation. A half dozen identical pieces of apparatus were then in operation, and specifications were easily obtained.

This method of testing flat sheets was adopted since fairly

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reproducible results could be obtained, and the type of cabinet represented the most popular method. The test consists of inserting the film between a dry atmosphere on one side produced in a cup by anhydrous calcium chloride and a humid atmosphere on the other side of the film maintained at 100° F. and 90-95 per cent relative humidity. After a 24-hour conditioning period, the samples are run for two 68-hour periods, the moisture pickup being measured by weighing the cup at the end of each time interval. The results are recorded as grams of moisture vapor transferred per 100 square inches per 24 hours.

This test gives a comparison between films as to the protection provided by a flat undamaged sheet. However, this value may be misleading if other factors are not taken into consideration. In forming a package, creases, sharp corners, seams, and closures are always present. These points are the most vulnerable part of any package. If the film being tested is coated or is slightly brittle, the film or coating may be cracked or damaged at the folds and sharp corners, or the seals may be a weak point. Therefore, films that show promise in the flat should be tested as packages to ensure that they will provide the same degree of protection when holding the product. The package can either be packed with the product under consideration, or with calcium chloride to accelerate the test.

Tests could be devised whereby the creased film is tested on a vapometer cup. This is being done at present, but little data are available. There is also a bit of uncertainty in interpreting this data.

After a film has proved satisfactory in a packaging test, shipping tests are undertaken if possible. They usually consist of shipping an experimental pack of the product under consideration to either a fort in the United States or to the Panama Canal Zone. However, since the war started, it has been increasingly difficult to get shipments or reports back from outside the United States.

The progress over the last year and a half in the development of flexible packaging materials has been slow but encouraging. The Quartermaster Corps today has several films that transfer less than one third of the moisture vapor transferred by our best sheets of a year or so ago. In one instance of a less strategic foil, we have a film with a moisturevapor transfer rate that is a small fraction of the best previously available.

Packaging presents itself as a picture of a ladder. At the top are the hermetically sealed metal cans; the other packaging materials are arranged on the ladder down to the materials offering least protection at the bottom. Just under the metal cans is a blank area, above some of the better fiber cans and specially laminated materials. Near the middle of the scale fall most of the moisture-vapor protective films. A line is drawn through this area marking the lower limit of the protective properties which a film may possess and still be suitable for army use. A great many films in domestic use today fall below this line. It is the blank area just below metal cans in which we are interested. We are searching for materials to fill the gap between the cans and the next best protective films.

Exceptionally strong shipping cases are required since the Army's food supply is expected to be transferred several times, subject to unloading at poor docks or on a beach, and exposed to rains and high humidities. Corrugated cartons, which are so popular domestically, have no place in overseas shipments. About a year ago, a weatherproof solid fiber board was developed which has fair resistance to rain and high humidities. However, this product is none too satisfactory and is used sparingly. At present, development of a better board is underway. Recently we have experimented with fiber boxes containing asphalt barriers and asphalt-impregnated sheets, as well as boards that have sisal fibers embedded in an asphalt barrier. These products show considerable promise, and further investigation is being carried out. Wooden boxes and wire-bound boxes have given the most satisfactory service and are now preferred for overseas shipment.

#### **Protection against gas**

The Army must be prepared at all times for attack with toxic gases. The nonpersistent gases are unlikely to damage food since it is difficult to obtain a high enough concentration for a long enough time to have a deleterious effect. The persistent gases are the ones which cause us concern. They are chiefly mustard and lewisite. We have investigated many packaging materials for their resistance to these gases, and the Chemical Warfare Service has tested practically all types of materials for gas protection. Many products have reasonable protection in the flat condition but poor protection at the folds, seams, and especially at sharp corners. Films that have been found to be most resistant to mustard gas are those employing protein, regenerated cellulose, and polyvinyl alcohol. Asphalt and wax provide less protection. Because of the poor protection that many films give at the sharp corners and folds, it has been necessary to obtain the most pliable films possible. This has been done by plasticizing the promising films. However, care must be taken that a plasticizer is not used that will dissolve mustard gas and, therefore, transfer it through the film.

Considerable protection can be given from mustard gas by employing packaging materials in several layers. It is interesting to note that the large family size cereal package is quite resistant to the penetration of mustard. This package apparently provides a combination of resistance to mustard gas in the waxed sheet and absorption of the liquid in the paperboard carton. Of course, hermetically sealed metal cans and sealed glass containers are completely resistant to mustard. At present our field rations C, D, and K are packaged so that they are resistant to contamination by war gases. Since it is difficult to obtain a single flexible film that is completely resistant to them, a combination of more than one film is required.

Attention has been given to the decontamination of gassed food supplies. It is almost out of the question to use the conventional bleaching agents on all food containers that might be affected. First, liquid mustard gas would be absorbed by the shipping cases, and it would be difficult for the bleaching agent to reach them. Secondly, considerable time, labor, and chemicals are required. Thirdly, it is undesirable to get the bleaching agents mixed with the food packages. Hence, the best attack is to protect the food in the first place so that it will not be contaminated. However, when contamination does occur, it is necessary to remove the outside case and destroy it. This makes it desirable to have an inner packing case that will carry the food products for a short time until the item is consumed.

If any one of the readers has or knows of a material that is being used for another purpose but might have extremely high moisture-vapor transfer resistance, the Quartermaster Corps would like to know about it. However, we feel that we have pretty well covered the present field of packaging films. We are not asking for a retest on present films or just a different combination. We are not interested in ordinary protection. We are calling on chemists for a superior product to do a stupendous job. Someone may have run across a product in the laboratory, probably in an entirely different application, that will lend itself to use as a packaging film with exceptional protective properties. That is what we want!

## Protection of foodstuffs against war gases

S. H. KATZ, Edgewood Arsenal, Md.

• • Chemical warfare agents in liquid or finely divided solid form are more likely to render foodstuffs unfit for use than those in gas or vapor form. As decontamination of the affected foods may be impossible, protection from contamination by war gases is the only method assuring that foods will remain wholesome.

Foodstuffs can be protected by suitable wrappings and coverings. Hermetically sealed metal, glass, or glazed earthenware containers provide perfect protection. Cellophane films are excellent. Multiple wrappings of dense sized paper, cellophane, waxed and coated papers are good. Corrugated paper cartons with abundant glue or sodium silicate in their structure are resistant. Seams, edges, and corners are points of weakness. Foodstuffs out-of-doors, whether unpacked or in containers, should be covered with paulins.

Some decontamination or salvage of affected foods may be possible. Foods contaminated with arsenicals must not be used unless unaffected parts can be separated from affected parts which must be condemned. Salvage and subsequent utilization of contaminated foods should be under the authority of medical or chemical warfare officers, or other qualified persons.

WHEN this paper was suggested, the subject "Decontamination of Foodstuffs" was proposed. This subject was not adopted because generally effective decontamination methods applicable to foods have not been developed—that is, methods that would leave the foods in wholesome and palatable condition. Prevention of contamination is therefore the best solution of the problem.

Specific test data on materials for protecting foodstuffs against chemical warfare agents have been generally withheld from publication through official restrictions the world over. Some general information has been published. However, the practical protection of foodstuffs against war gases can be accomplished by the use of many common materials and involves no very technical procedures. Many foods are well protected by the packages in which they are marketed.

#### Mechanism of contamination

Chemical warfare agents employed for their toxic or other severe physiological effects are mainly organic compounds, frequently halogenated. Sulfur, nitrogen, and arsenic characterize some very potent agents. Inorganic chemicals have a part in chemical warfare, mainly in smoke screen materials and in incendiaries. White phosphorus, employed as a smoke-producing agent, is toxic; if it is dispersed from a shell bursting near foodstuffs, the foodstuffs may become unusable.

Major problems of protection, or of decontamination, arise from toxic agents in the liquid droplet form, dispersed from projectiles or from airplanes, or agents in the form of solids subdivided into dusts or dispersed as smokes. The gaseous or vapor forms are more transitory or "nonpersistent". Although foods should not be exposed to the agents in gaseous form, contamination from such war gases will usually be less severe than contamination with liquids or dusts unless exposure of absorbent foods to the gases is unusually prolonged.

Some types of foodstuffs accept contaminants much more readily than others. Butter is prone to absorb vapors from other foods. The same is true with butter exposed to vapors of chemical warfare agents, and other fatty foods act similarly Vegetable foods in natural form are more resistant to contamination from vapors. The liquid and finely divided solid agents readily contaminate any foodstuffs if they are unprotected and contact occurs.

#### Decontamination

Decontamination of matériel in general is conveniently accomplished by chemical methods. The decontaminating agents chlorinate, oxidize, hydrolyze, or otherwise react with the war gases so as to destroy their militarily useful properties. Chloride of lime is an inexpensive decontaminating agent and finds much use. But reaction products are not eradicated by decontamination, and the products may be poisonous if eaten with foods. They would be unpalatable and certainly unwholesome. Most decontaminating agents are themselves toxic or at least unfit for consumption. The decontaminating agents are customarily applied in excess to assure a sufficiency of the decontaminant and to obtain the benefit of mass action. Some decontaminants react with constituents of foods.

In the instance of the arsenical war gases, the molecules bearing the arsenic are destroyed by the action of decontaminants but the arsenic remains toxic in some secondary chemical combination. Water alone will hydrolyze some of the arsenicals—for instance, lewisite. Foods contaminated with the arsenicals cannot again be made fit for consumption. It may, however, be possible to separate uncontaminated portions from contaminated parts and utilize the uncontaminated parts.

All war gases, however, do not render foodstuffs hopelessly useless. For instance, phosgene and chlorine are removed to some extent by ventilation, heating accelerates the removal, and cooking will completely destroy any small residual amounts of these agents by hydrolysis (7).

#### **Protection of foods**

Since decontamination of foodstuffs is frequently impractical or impossible, the problem of maintaining supplies of in i

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wholesome foodstuffs when they are subject to attack by war rases becomes one of protecting the foodstuffs from contact with the gases. Fortunately this is not difficult, since many types of commercial packaging materials and packages provide effective protection.

HERMETICALLY SEALED PACKAGES. Sealed metal, glazed earthenware, or glass containers completely prevent contamination of their contents by war gases in any of their physical states or forms. The sealed containers may become contaminated on their outer surfaces. They can be purified by immersion for half an hour in boiling water and then rinsing. If the contaminant is a vesicant, the persons handling the containers should be protected by impervious clothing and gloves, and should wear gas masks.

CARTONS. Numerous foods are supplied in cartons comprising several layers of dense paper, waxed paper, cellophane, or other manufactured films in various combinations. Many of the multilayer packages provide effective protection for their contents. Unbroken metal foils are completely impervious. Cellophane has outstanding resistance to penetration. If the outer coverings of foods packaged in resistant materials become contaminated with liquid chemical warfare agents, the contaminated coverings should be removed and the food transferred to other uncontaminated containers. Superior types of packages will resist the penetration of liquid agents for hours or even days. However, the foodstuffs should be transferred from contaminated cartons as soon as possible to obviate later contamination when penetration finally may occur. Seams, edges, and corners of cartons are the portions most susceptible to penetration because they are subject to breakage or lesser damage.

MULTILAYER CONSTRUCTION. Multilayer material in cartons, providing some air space between layers, is more resistant to penetration by liquid chemical agents than a single layer of the material of thickness equal to the total thickness of multilayer material.

BAGS. Ordinary paper bags of single thickness are not

resistant to penetration by liquids. Most papers are porous and readily absorb and transmit liquids. Multilayer bags or sacks of special construction, holding about a bushel, are made. They protect well against war gases and may become standard equipment if needed. The plies are composed of dense kraft paper laminated in pairs with asphalt binder. Cellophane is included in some plies. The multilayer bags are specially suitable for vegetables or for holding a variety of smaller packages or articles of any kind. Grain for horses and mules may be well protected in such bags.

PAULINS. Paulins of large size are convenient protective coverings for bulk foodstuffs for men or animals when it is necessary to transport, handle, or store the foods in open air. Paulins protect from the weather as well as from the gases. They serve as auxiliary protection for contents of boxes or bags out-of-doors. The paulins may be canvas impregnated with a variety of substances such as drying oils, synthetic resins, rubber, or rubber substitutes. They may be laminated with a layer of impervious material between layers of fabric, or fabric may be coated with the impervious material. In any construction they should be treated to prevent rapid absorption of liquid into the cloth coverings of impermeable layers.

Food must be protected from liquid spray or toxic smokes while in army kitchens and when being distributed to front positions. Tentage, paulins, or smaller coverings serve the purposes. Even untreated fabric, prone to absorb liquids and become wet through, can protect against falling drops or liquid splashes, if woven tightly enough to prevent passage of spray, and located to avoid contacting the protected materials.

#### **Protective materials**

Many types of materials employed in protective coverings have been mentioned previously. Unique properties of some materials, apart from the structures of coverings in which they are employed, may be considered.



Field Rations in Gasproof Packages

Photo by U. S. Army Signal Corps

Vol. 35, No. 1



Photo by U. S. Army Signal Corps Corned Beef in Metal Cans and Dry Milk in Gasproof Drums

METAL FOILS. Metal foils, such as tin, aluminum, and lead, are familiar in small packages of confectionery and tobacco. When perfect, the foils are completely impervious to the war gases in any form. Weaknesses lie in the corners and edges of packages where breakage of the foils is prone to occur. Pores may exist. Packages should be tightly sealed. Foils laminated to strong papers are more durable than unlaminated foils. Foil wrappings, completely impervious to gases and perfectly sealed, permit no passage of air. Such wrappings in air transport may burst at higher altitudes because of excessive internal air pressure. Wrappings containing foil have been considered for first-aid bandages. Metal foils are most suitable for small-sized packages.

CELLOPHANE. Among the organic wrapping materials, cellophane or regenerated cellulose has exceptional resistance. Strength may be provided by laminating it to strong papers or fabric. Cellophane alone lacks a desirable degree of elasticity, and tends toward brittleness and low tear strength. Plasticizers eliminate the brittleness and improve elasticity, but reduce resistance to penetration of liquid agents. Moderate amounts of plasticizer give desirable properties and can be tolerated. POLYVINYL ALCOHOL. PVA has unusually good resistance to chemical warfare agents and makes a fairly tough film. Some plasticizer is required to impart a desirable flexibility. PVA is hydrophylic and may be dispersed in warm water; hence it should be protected from moisture by combination with other wrappings or coatings. PVA films have not yet been employed for food coverings.

GELATIN-GLYCEROL. This combination of gelatin with glycerol plasticizer to impart flexibility is very resistant. Treatment with formaldehyde or chromates is needed to make the gelatin insoluble in water. Glue can take the place of gelatin in paulins where the glue-glycerol is used as the inner layer between cloth laminations. Resinous varnish coatings on the outer surfaces prevent absorption of liquids by the cloth.

PAPER. Most papers are porous, but the densest forms such as parchment papers have considerable merit. Glue sizing improves resistance. Coatings of varnish or resinous materials add their own superior resistance to that of the paper. Sizings in the heavy cardboards can improve them greatly. Corrugated papers adhered with abundant sodium silicate or glue on inner surfaces make resistant boxes. Freas and West (3) state that, during World War I, tar paper furnished "one of the cheapest and most available means" of protecting foods. Tar paper would not, however, be suitable for foods that absorb tarry odors unless some intermediate protection against the odors were included in the coverings.

SYNTHETIC RESINS. Wrapping materials in sheet or film form are produced from many types of synthetic resins. Resistances are variable but use may be made of many types. Their lacquers or varnishes can be utilized in coatings or for laminating other materials. Materials that may be employed are cellulose acetate

and the butyrate copolymer; cellulose nitrate; vinyl chloride, acetate, butyrate, and their copolymers; ethylcellulose; glyptals; phenol-formaldehyde and urea-formaldehyde types. Nylon films when commercially available will be excellent. Vinylidene chloride and the new melamine-formaldehyde resins are good.

RUBBER AND SYNTHETIC RUBBERS are particularly suitable in paulins. Natural rubber is less resistant than the synthetics. Their resistances to war gases are comparable to their resistances to petroleum oils (where the synthetics are superior to the natural). All of the synthetic rubbers now or soon to be available are valuable protective materials: Thiokol, neoprene, Vistanex, Buna types, and Butyl rubber; the latter will be an exceedingly valuable addition when available.

#### **Testing impermeable materials**

Precise details of the method of testing impermeable materials for resistance to penetration by liquid chemical warfare agents or of the apparatus employed may not be divulged. But a general description of the test with mustard may be given  $(\vartheta)$ : 100

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A circular sample of the material is sealed between the flanged edges of two suitable glass cups. The upper cup has a tubulure through which 5 drops (0.12 gram) of liquid mustard are placed upon the center of the material. The liquid is permitted to spread naturally. The lower cup has two tube connections, dia-metrically opposite. Air is passed through the lower cup at the rate of 200 cc. per minute and then bubbles through an absorber bedding. Congo red indicator solution. When mustard penetreter rate of 200 cc. per minute and then bubbles through an absorber holding Congo red indicator solution. When mustard penetrates the sample, it vaporizes into the air stream, passes to, and hydrolyzes in the indicator solution where an acid reaction is recognized. The time for penetration to occur, as shown by the indicator, is taken as a measure of the resistance of the sample.

#### Salvaging contaminated foods

Dry foods exposed to gases or vapors and then aired until no odor of the agent remains may be consumed after cooking. This applies to beans, peas, rice, coffee, desiccated vegetables or fruits, and the like. Sartori (8) states that the drier foodstuffs exposed to phosgene can be made wholesome by exposure to a current of warm air. Moist or fatty foods must be regarded as unsafe after exposure although the particular gas, when it is known, may indicate whether consumption is permissible or not. Moist foods exposed to arsenicals should not be eaten. Phosgene hydrolyzes in water to form hydrochloric acid. The amounts of hydrochloric acid developed after most conditions of exposure would not be sufficient to vitiate the foods. An instance occurred in the United States in 1918 when a shipment of foods was exposed to phosgene; live chickens were present and some died. The foods included crated raspberries, green beans in their pods and cabbage. When the foods were examined a few hours after exposure, they retained no odor or foreign tastes and were safely consumed.

Hanslian (4), relating German experience in World War I, said: "after exposure to clouds of gas, food took on a slight odor of the gas, which it generally lost after being aired It could be eaten without hesitation. On and cooked. the contrary, the eating of food which had come in contact with shell splinters or the liquid contents of gas shells, or even with drops falling from thick gas clouds, was injurious



Photo by U. S. Army Signal Corps Beans in Gasproof Sacks (Sacks at Lower Right Are Not Gasproof)

to the health and therefore condemned even if no odor was perceptible."

Droplets of mustard on meat will penetrate no further than 4 to 5 mm. in 48 hours (6, 13). Carcass meat contaminated with drops of liquid mustard might be consumed in emergency, if the contaminated outer parts were cut away (12) to about one-half inch depth and discarded, and the remaining part was thoroughly boiled. Boiling hydrolyzes mustard. Contaminated parts must be cut from a carcass in such a manner that the knife transfers no mustard from the outer contaminated parts to the inner portions. Sliced meats contaminated with mustard must be discarded.

Foods exposed to war gases should not be utilized for consumption until inspected and released by a medical officer (10, 11), a qualified chemical warfare officer, or other qualified and responsible persons. They may have testing equipment (1, 5) or the facilities of a chemical laboratory. A detailed scheme for detecting war gases in foods has been published (2). If no artificial means of testing are available and the contaminant is known, the senses of smell and taste may be resorted to in cases of extreme need.

The official directions of the War Department (11) pertaining to the reclamation of contaminated food supplies are quoted below:

The most effective and practical measures for purifying foods, forage, and grain contaminated by chemical agents include trimming of exposed surfaces, complete aeration or ventilation, and hydrolytic procedures, such as boiling in water or washing in dilute (5 per cent) bicarbonate of soda solution. Even these measures may be ineffective if the decomposition products are

themselves toxic, as in the case of lewisite. b. In general, food, forage, or grain exposed to low vapor con-centrations of chemical agents can be reclaimed by the procedures listed above. It is impracticable to reclaim provisions that have been heavily contaminated by vapors, droplets, or dusts, espe-cially of the vesicants, arsenicals, or those agents which upon hydrolysis split off other toxic compounds. Highly contaminated supplies, such as those on which chemical agents can be seen with the upon idea of the considered encided and their dust. the unaided eye, should be considered spoiled and their decon-tamination or purification impracticable. c. While recognizing difficulties of decontamination proced-ures, it is nevertheless realized that it may be necessary or even

mandatory to use these measures under certain tactical or economic conditions, particularly when there is a marked shortage economic conditions, particularly when there is a marked shortage of foodstuffs or where great losses of salvable products are in-volved. After reclaiming foods, especially those of high fat con-tent, contaminated with the highly acid gases, the taste of such products may be greatly impaired, although the energy content of the foods is not altered. It must be emphasized that the use of any decontamination procedure will be greatly complicated when foodstuffs have hear exposed simultaneously to the action of foodstuffs have been exposed simultaneously to the action of more than one type of chemical agent.

d. When it is necessary to use animals for food following their exposure to lung irritant gases, the carcass meat may be con-sumed if slaughtering has been done in an approved manner, even while pulmonary injury is still active, provided the other internal organs are normal, since even animals fatally poisoned by these gases die before the agent spreads throughout the carcass meat. Portions of carcass meat directly under the skin areas affected by vesicants should be discarded.

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# Nutritional aspects of food processing

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• • • The establishment of nutritional standards that include labile and soluble nutrients presents new problems in attaining an adequate dietary that have repercussions in the processing of foods. Procedures in processing may result in significant modification of the original nutritive value. The known nutrients particularly concerned are carotene, ascorbic acid, thiamine, protein, and, in some cases, soluble inorganic salts. Where processing causes considerable destruction, the consumer must look elsewhere for those nutrients. Failure of the consumer to recognize the significance of these losses may result in malnutrition in cases where the foods form an appreciable part of well established habits. Evidence is accumulating to show that there are considerable losses in nutrients in the preparation and service of foods in general.

Processors can profitably show the nutritive value of foods as marketed and the consequences of improper handling in preparation and serving. They can advise on the best ways of preparing food to conserve the maximum nutritive value. To do this, the changes in nutritive value from the time food reaches the processor until it is consumed must be known.

THIS war has brought to the fore new nutritional problems. They are important to the public as well as to the armed forces. The most difficult ones arise from the lability of certain nutrients, particularly carotene, thiamine, and ascorbic acid, and from the water solubility of members of the vitamin B complex and of certain inorganic elements. The crux of these problems is "conservation of nutrients" in our food. The world-wide extent of military operations introduces additional problems of logistics, including the nature and character of food for overseas operations in general and for special tasks. Processed foods are the key to some operations. The priorities for metals precipitated by the war effort have superimposed new problems of successful packaging.

Foods are processed for three major purposes: (1) to preserve them against deterioration, (2) to create new products of increased appetite appeal or of specific nutritive value, and more recently, (3) to prepare food combinations for the convenience of those who do not have the time, skill, or opportunity to make them from raw ingredients. The chief means of preserving foods are by dehydration, sophistication (purified foods), heat, cold, combination with other foods such as sugar and spices, and packaging. In most of these processes the original nutritive value of the food is modified. According to the method of packaging and storage, further deterioration may or may not take place. Processed foods may contribute or be a potential detriment to the health of the nation, depending upon whether or not they are used in the daily dietary with due regard to their nutritive values.

We are creatures of habit, particularly with regard to food. Food habits have developed as the result of experience and custom which may have their roots in the past long before our sophisticated foods were devised. In general, these habits have given us a fair state of nutrition. The introduction of "purified" or processed foods (such as in the case of patent flour combined with the consumption of fat back in our South, polished rice in some parts of the Orient, corn meal in Italy, and the general use of condensed milk and certain cereal preparations as the major food for babies) has been accompanied by a significant incidence of malnutrition. These innovations were introduced before the vitamins were known. The difficulties encountered in correcting these conditions is evidence of the force of habit. For example, it has required action of the Food and Nutrition Board of the National Research Council, the cooperation of the millers, and now legislative action such as that in North Carolina and Louisiana to bring about the correction of difficulties encountered in the case of white flour.

The establishment by the Food and Nutrition Board of tentative nutritional allowances has presented to the armed forces and the public the problem of attaining them. They have provoked and increased a general interest in the nutritive value of foods, in variations to be expected in the same food, and in the extent to which the labile nutritive factors, such as carotene or vitamin A, thiamine, riboflavin, ascorbic acid, and the biological values of proteins, are retained or destroyed in the course of harvesting, processing, storage, and preparation for the table. It will no longer suffice to assume the dietary is adequate because a wide variety of foods has been provided. The quality and quantities of the various loods consumed become a part of the evaluation. The consumption of sufficient quantities of a few well selected and prepared foods may provide a dietary as adequate as that obtained from a wide variety of foods consumed in small quantities. In fact, many of us live on a relatively restricted dietary.

WHAT is the significance of recent developments in nutrition to food processors? Primarily, since changes occur in the nutritive value in processing foods or in storage of processed foods, these changes should be reduced to a minimum, and where they do occur they should be determined and the public informed about the final nutritive value of the products. The National Research Council's nutritional allowances are a statement of nutritive requirements. They refer to the food as consumed and not as purchased. It is important, therefore, to know the losses of the labile nutrients which occur in the ordinary manipulations of cooking and standing after and and

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cooking, the extent to which they occur in the liquors of processed foods, the best way of using these liquors, the leaching that occurs in reconstituting dehydrated foods, the deterioration of foods due to oxidation and climatic conditions when they are not protected by adequate packaging. Recent evidence has confirmed older observations that the losses in nutritive value of foods on standing after they have been cooked may be fully as great as during cooking.

Who should provide this information? It seems that the food processor should do it for his own protection. The canning industry is in an admirable position to do so because some years ago it demonstrated that ascorbic acid was retained to a considerable degree in the canning of most vegetables and fruits and that properly processed canned foods compared well with similar foods purchased in the market where these foods had lost nutritive value in the course of marketing and the ordinary process of preparation in the home. There still remains much to be done to ensure the retention of nutritive values in a larger proportion of canned foods. The canners are not content with the information at hand and have initiated a study to determine the variability of similar foods in different parts of the country and after storage. In this regard, we are reliably informed that in Australia the minimum vitamin C content of canned vegetables and fruits will be required to be clearly stated on the label. In spite of the information we possess with regard to canned foods, there is a general feeling that the dietary is inadequate unless fresh foods are available. Part of this attitude is explained in relation to the greater acceptability of fresh foods and in part from a failure to consider inherent nutritive values. The frozen food industry is likewise in a preferred position as the result of investigation of the nutritive value of fresh frozen foods and the conditions for their use. The meat industry is engaged in a series of projects to show the extent to which labile nutrients are retained in the process of cooking. The enrichment program for flour will supply information on the variability of wheat.

Where special claims of nutritive value are made on the label, the Food, Drug, and Cosmetic Act requires that certain supporting information must be supplied. The standards set up are minimum and differ from the allowances of the Food and Nutrition Board. In this connection it is important in discussing foods to differentiate between the minimum requirements set up under the act and the tentative allowances of the Food and Nutrition Board. For instance, definite confusion has arisen in one case because in one part of the literature the nutritional allowances of the Food and Nutrition Board are given, while in another part the nutritive value of foods is presented in relation to the minimum standards of the Food, Drug, and Cosmetic Act. The result is likely to lead to a feeling of false security in relation to the total dietary and points to the need for clearly defined statements with regard to nutritive values.

THE importance of a sound background of information with regard to the nutritive values of foods is illustrated daily in the Surgeon General's office, and in the headquarters of various service commands and camps where it is necessary to review the messing operations of the Army and to consider whether or not the food provided contains nutrients in sufficient quantities to maintain a healthy efficient soldier. A comparative review of messing operations in training camps during the first and second World Wars indicates that there is little difference, with the exception in some cases of milk, in the kinds and amounts of food consumed. This means that if the soldier today is better fed than in 1918–19, it is largely because we know more about conserving nutrients in the preparation and service of food.

The problem of processed foods is not so acute for the armed forces in this country as it is in relation to rations for expeditionary forces. The need to use foods that do not require refrigeration and the necessity to save space and tonnage have presented some serious questions in regard to the nutritive value of processed foods. It is the general policy of the Army to provide the various nutrients in the food itself rather than to turn to substitutes such as vitamin concentrates. This attitude is desirable for two reasons: (1) food is a matter of morale and in this respect has more to do with the dietary habits of the soldier than with nutrition per se; and (2) while it is possible to provide certain purified or synthetic nutrients, in the light of our present knowledge it is still necessary to depend on natural, unsophisticated foods for other unknown accessory food factors.

The problems of the Army in relation to changes in nutritive value relate largely to carotene or vitamin A, thiamine, ascorbic acid, and riboflavin. The high temperature and time required to sterilize meats, from which the soldier normally obtains half his thiamine, tends to destroy thiamine. The methods of dehydration of vegetables, while progressing. have not advanced far enough to make them reliable sources of ascorbic acid and carotene or vitamin A. While some processes are rather successful, the evidence so far does not justify the assumption that the general run of such products is dependable. Dehydrated potatoes, for example, are practically devoid of ascorbic acid. It is not known what the losses of ascorbic acid and carotene of other vegetables will be after storage for six months to a year. Natural citrus products when concentrated have not been particularly stable when kept without refrigeration. Furthermore, we can only speculate on the vitamin content of foods after they have been reconstituted and cooked in the average army kitchen.

BECAUSE of the difficulties presented by processed foods, it has been necessary to resort to lemon powders in addition to canned vegetables and fruits to assure an adequate source of ascorbic acid. Enriched flour and bread have helped compensate for the losses in thiamine. While there is some indication that the nutritive value of the proteins is impaired in canning, this is not so serious since a certain amount of milk and egg products dried at low temperatures is provided. The special rations, such as the Type C ration with its meat components of canned stew, meat and beans, or meat hash, and the Type K pocket ration, all require frequent checking as to nutritive value.

These problems of the Army are discussed because they are so important and obvious. The conditions that exist in the Army may become problems of the civil population if it is required to use increased quantities of inferior dehydrated foods. Should this be true, the possibilities of malnutrition may be serious, since the public will not have the advantage of the careful review of the adequacy of its dietaries that is given the rations of the soldier.

The difficulties of processing have been emphasized rather than the advantages, such as the increased availability and variety of foods throughout the year, in order to bring out the point that it is not sufficient to produce an attractive product. It is equally important to conserve the maximum nutritive value of the natural product. If there are considerable losses, the consumer should be informed of the facts This means that along with the technical developments of the industry should go research on the nutritive value of those foods, not only of the canned or packed product but also of the food as it will be consumed. The latter information should include both desirable and undesirable methods of preparation. Comparison with the usual methods of preparation of fresh foods will often be valuable in demonstrating the advantages of the particular process. Such information properly presented will result in confidence in the product and lead the consumer to use it in the total dietary

### Freezing foods

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• • Problems of variety and maturity must be solved in order to obtain a satisfactory frozen product. Quality control is important to the future of the industry. Expansion in the industry has led to new sites of food production in order to supply the raw product. Under present conditions, the frozen food industry can play an important part in the war effort by preserving perishable foodstuffs which might otherwise be lost.

**CODAY** the frozen food industry, like any other, is faced with the problem of how it is best fitted to meet the war emergency. Since it is involved in the preservation of foodstuffs, it can assume an important position. "Statistics collected by Food Industries indicate that the 1940 production in the United States amounted to 555,881,000 pounds: that for 1941, 697,481,000 pounds; and the anticipated 1942 production, 823,931,000 pounds. These figures include production of cold-pack fruits and quick-frozen fruits, vegetables, meats, fish and poultry" (4). It should be noted that the above figures do not include meat frozen for storage, frozen eggs, frozen cream, uneviscerated frozen poultry, or fish frozen in bulk. Nor do they include the output of some 4500 locker plants scattered throughout the country. Table I indicates the relative amounts of the various frozen foods packed.

Table I. Quantities of Uni	Foods Fro ted States	ozen Annually in th 3
Product	Year	Quantity
Butter	1937	200,000,000 lb.
40%	1937	1,000,000 gal.
Eggs	1937	300,000,000 lb.
Fish Fruit	1939	202,307,701 lb.
Ice cream Meat	1937	243,551,000 gal.
Beef Lamb and mutton	1937 1937	199,548,000 lb. 11.027.000 lb.
Pork	1937	511,604,000 lb.
Shellfish	1939	20,482,000 lb.
Vegetables	1941	107,190,012 lb.

In conjunction with these production figures, *Food Industries* lists twelve different types of freezing methods now in use. What the industry could do if pushed to the limit is a point of conjecture, but with full utilization of storages and some equipment conversions, the amount could be substantially increased.

At present the United States Army is buying large quantities of frozen boneless beef. A ton of beef carcasses occupies 100 cubic feet. After boning and packing into containers for freezing, it occupies only 35 cubic feet. Owing to the resultant conservation of shipping space and weight and to the rapid increase in the size of our army, it is probable that much larger amounts of beef and other meats will be boned, packaged, and frozen for army use in the near future.

Due to the shortage of tin and the necessity for other means of supplementing the food supply, methods of food preservation other than canning will become increasingly important. the longer the present conflict continues. As far as home demands are concerned, the freezing preservation of food can help to solve the problem of supplying nutritious, palatable food preserved with a minimum of essential materials. Also, since the canning of certain products has been curtailed by government decree, there is opened to other means of food preservation, such as freezing, the possibility of continuing to make available carrots, beets, sauerkraut, baked beans, and many other foodstuffs.

Another way in which the war is affecting the frozen food industry is in the amount and kinds of fish available. Fishing boats do not cover the same range as in peacetime, and many of the ships are performing duties other than fishing. Even before the war the fish fillet situation became so acute that the red perch or rose fish had to be used.

#### Variety studies in various localities

Another factor which is having an effect on frozen foods, although it is not a direct outgrowth of the war, is the frozen berry situation. From all indications berry freezing in Oregon and Washington has about reached its productive capacity. Recently the industry started to expand in the South, especially in Tennessee. Coupled with availability of the fruit, there is an increasing demand for frozen fruits for making pectinized purées to be used in ice cream manufacture. The need for varieties suitable for freezing which will do well in New York prompted the variety studies being conducted at this laboratory for the past ten years. Table II contains in abbreviated form some of the conclusions of this study.

 
 Table II.
 Varieties of Fruits Satisfactory for Freezing in New York State

STRAWBERRIES	RASPBERRIES	PEACHES
New Jersey 225 Redheart Senator Dunlap Minnesota 1192 Van Rouge	Red Cuthbert Viking Milton (N. Y. 13618) Purple Columbian Sodus Marion Black Bristol	Yellow Hale Haven South Haven J. H. Hale Elberta Ideal Vedette Veteran Viceroy Summercrest

Experience so far has shown that none of the varieties of strawberries grown in New York in large quantities will, when frozen, compare with the Oregon-grown Marshall; nor will any New York-grown raspberry rival the Cuthbert of January, 1943

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#### Careful Inspection of Peas to Ensure a High-Quality Frozen Product

The peas are first put through a washer (above). After passing through a quality grader in which the overmature peas are eliminated, those of optimum maturity are put into stainless steel buckets (*left*) in which they are taken to the inspection belt. Blanched peas are inspected (*below*) prior to packaging and freezing; yellow and split peas and skins are discarded.

sulting harmful effects may take years to correct at a later date.

#### Quality control

Quality control means following the article from seed to finished product. Proper quality control will result in a product acceptable to the ultimate consumer. Proper quality control maintained by chemists and other qualified technical men will help determine the ultimate fate of the frozen food industry; for as long as standards are made and adhered to by the industry through these men, the products are likely to be accepted by the general public.

the West Coast. The Elberta peach is the most important variety grown in New York in sufficient quantities for commercial freezing. It is a fair to good peach when properly matured on the tree. However, due to methods of picking whereby the tree is "stripped", a percentage of unripe or box-ripened peaches is included in the pack which is not so satisfactory. If Elberta peaches are held in cool storage and then processed, a flavorless, "punky" product of indifferent quality is produced.

Often fruits or vegetables considered excellent in one locality have proved only fair or inferior when tested under New York conditions. The point of proper varieties for the region in which they are grown cannot be overemphasized. The idea is prevalent, even among people in responsible government positions, that any fruit or vegetable variety will give an excellent product when frozen. If such an attitude is forced on the frozen food industry, it is possible that the re-



RAW PRODUCT. The control of the raw product involves micro- and macroscopic examination for insects and insect injury. In addition, the raw foodstuff must be inspected for general appearance and, in the case of such products as peas, corn, and lima beans, for maturity. At this point the chemist is faced with a problem which has not yet been satisfactorily solved. The Tenderometer has found a definite place in the evaluation of raw peas in that it is recognized generally that raw peas with a maximum value cannot be frozen and meet the government specifications of fancy grade. However, although there is a maximum value, the condition often arises where peas on the threshold may or may not separate to give the desired product. Corn for freezing or canning is ordinarily evaluated essentially by either a thumbnail test or by a total solids determination of some kind. Neither of these tests has proved infallible due to several conditions. Jenkins and Lee (5) suggested the Tenderometer for the evaluation of raw asparagus. However, the fact must be faced that fundamentally there is no basic information on what particular constituents might be measured to give a relatively rapid and accurate index of the raw product maturity.

PACKAGING. The importance of gastight, moistureproof containers for the prevention of deterioration through dehydration, contamination, and oxidation is well recognized by the industry. Under present conditions frozen food manufacturers are more fortunate than other food preservers in that there seems to be sufficient supply of moisture- and vaporproof types of cellophane papers. It is unfortunate that the shortage of rubber has curtailed the availability of rubber composition papers and latex bags, especially since these bags were rapidly coming into use in poultry and in some kinds of fruit freezing. Work along the lines done by DuBois and Tressler (1) on proper papers for freezing can serve as an index to the best wrapping materials to be used. The two fundamentals of proper packaging might be said to be a good paper and an effective seal.

STORAGE. Experience has shown that most fruits and vegetables can be held satisfactorily at 5° F., although 0° F. is preferable. DuBois, Tressler, and Fenton (2) indicate the importance of low-temperature storage for maintaining the original quality of meat. They demonstrated that meat held at 0° F. maintained its fresh flavor for about a year, while meat held at 10° and 15° F. did not stay fresh for more than 6 months. It is an interesting digression to note that when frozen beef is to be used in the type C army ration, the meat cannot have been stored for more than 180 days. The army specifications for holding beef recommend 0° F. or lower but allow for a maximum temperature of 10° F. for short periods. In a study of holding temperatures for frozen poultry, DuBois et al. (3) showed that at 10° F. the maximum safe holding time is about 4 months; at 0° F. it is about 6 to 12 months, depending on the package and method of preparing the bird. At  $-8^{\circ}$  F. the undrawn, properly wrapped chickens retain normal flavor after storage for 20 months.

Jenkins, Tressler, et al. (6) demonstrated that, in frozen vegetables studied by them, none showed any vitamin C loss after storage at  $-40^{\circ}$  F. and little or no loss at  $0^{\circ}$  F. Storage temperatures of 10° and 15° F. caused serious losses in relatively short times.

Most frozen products still have a potential enzymic system which can act at ordinary storage temperatures. Joslyn (7) attributed flavor and other losses in some of the vegetables, which do not keep so well as they might in frozen storage, to the presence of peroxidaselike enzymes which are not completely inactivated by the usual blanching practices. The rancidity of fats in cold storage poses a problem for the chemist in that work is needed on tests for incipient rancidity.

EVALUATION OF FINISHED PRODUCT. The Agricultural Marketing Service of the United States Department of Agriculture has been setting up standards and intends to enlarge the work on the formulation of grades and standards for frozen products. At this writing they have issued either tentative or final standards on corn, asparagus, peas, lima beans, and frozen cherries, and have carried out experimental work on broccoli, spinach, Brussels sprouts, snap beans. cauliflower, strawberries, raspberries, and sliced peaches

These tests in most cases are more or less based on four principal factors: color, flavor, physical defects, and maturity. Good varieties properly handled will take care of color, flavor, and physical defects. Maturity, as in the case of peas, is determined by a sinker test, which is essentially a specific gravity determination. With corn there is a sinker type test and a residual sugar test; this will undoubtedly provide not only an index of maturity but also the conditions under which the corn was held prior to freezing. Lee (8) and Lee, DeFelice, and Jenkins (9) used a specific gravity test based on the principle of Archimedes. With a little refinement in technique, this type of test may find a place in the routine quality control of frozen products.

#### The future

The importance of quality cannot be stressed too greatly, for upon this factor depends final consumer acceptance, and upon consumer acceptance rests the future of the frozen food industry.

As long as we are involved in total war, every pound of perishable food which can be frozen and utilized in this country means that more tinned goods can be made available for our soldiers and allies in distant lands. The frozen food industry, therefore, has the potential task of helping to feed institutions, hospitals, and army camps as well as the general public. The maintenance of morale through proper nutrition has been stressed over and over. Proper nutrition means an available supply of food properly handled and preserved to retain the maximum nutritive value. The frozen food industry will continue to aid in the war effort by preserving large quantities of high-quality food, both from the standpoint of palatability and nutritive value.

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### Cold storage of food

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Airplane View of Atlantic States Warehouse and Cold Storage Corporation

• • The laws of the different states pertaining to the cold storage of food are summarized. Comparative charts show the variation in storage holdings from 1917 to 1925 and from 1928 to date. The charts indicate holdings in the United States of various articles of food in cold storage warehouses.

A short account is given of the value of cold storage in preventing the spread of certain parasitic diseases. Possible changes which may occur in cold storage are indicated.

Cold storage is a necessary part of our civilization. In the winter we can have berries grown six months prior and green peas as good as when picked from the vine. People in the Midwest can obtain fish fillets frozen within a few hours after they were caught. Frozen meats can be shipped long distances to localities which are largely industrial. Cold storage operations will probably exercise a still greater influence over the production and cost to the ultimate consumer of perishable foods.

THERE is nothing particularly new in the cold storage business, and it is not entirely confined to highly civilized people. Certain of the Eskimo tribes catch wild birds in the springtime, place the carcasses in caves of perpetual ice, and eat the carcasses in the winter when fresh meat is scarce. It is also a practice in some farming communities to slaughter a steer in winter, cut up the meat, allow it to freeze, and keep it frozen in a shed for consumption from time to time during the winter season.

The commercial cold storage of food is a business operated for the purpose of making a profit and is a necessary part of our present economic system. The fundamental economic principle involved is the preservation of surplus perishable foods, produced in quantities too large for immediate consumption, to be released when there is a scarcity of the food so stored.

Cold storage of food produces an equalization of wholesale prices and also stimulates production. If we did not demand eggs during November when the production of eggs is curtailed, there would be no incentive to raise surplus eggs in the spring months; but if there were no means to store the surplus eggs produced in the spring, it would for practical purposes be impossible to consume them before they spoiled.

Laws are placed upon the books because a few people abuse privileges not covered by existing statutes, and our cold storage laws were enacted for that reason. Even today there is some violation of the law relating to the sale of cold storage eggs, possibly because during the early fall months such eggs can often successfully masquerade as fresh.

#### Legislative reports on cold storage

The Massachusetts Cold Storage Law was enacted after a thorough study by a recess legislative committee appointed in 1911. The report of that committee (7) is a remarkably complete document upon the business of cold storage. The report deals in part with economic aspects, and discusses retail and wholesale prices over a period of years. It contains an appendix covering the cold storage legislation in existence at that time in the United States and Canada.

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Another legislative document (1) contains many facts and considerable demagogy relating to cold storage. No legislation of a national character resulted, and there is no national cold storage law today. In discussing this question in 1926 I stated: "Such a law is desirable and almost necessary ..... The United States Food Law, however, should be amended to contain a provision regarding sanitation, which could then be applied to cold storage as well as to other phases of food preparation and handling" (5). The United States Food, Drug, and Cosmetic Act of 1938 contains provisions regarding sanitation in the food industry, and, therefore, the necessity for a federal cold storage law is not now so great as it was twenty years ago.

#### **Result of recent questionnaire**

A letter was recently sent to each state requesting a copy of their cold storage law, if any, and comments thereon. The replies show that twenty-two states have no such law. Seventeen have a general cold storage law; one has a law by regulation made under a special act of the legislature; one has a law pertaining only to the licensing of warehouses; one has a law pertaining to removal of entrails from cold storage poultry as well as from other carcasses prior to sale; and six have cold storage laws regulating only the sale of cold storage eggs. The cold storage law of North Dakota was repealed in 1940, but the plants are inspected under the sanitary inspection law. One reply stated that the creamery men killed the attempts to obtain a cold storage law, but sanitary inspections are made by the state food and drug department. Another state replied optimistically that probably the next legislature will pass such a law. The following is quoted from a letter by A. M. G. Soule of the Maine Department of Agriculture:

The writer has made two unsuccessful attempts to have a Maine Legislature enact such a law. It is based largely on the best features of your Massachusetts law, but the packers decided they did not want the legislature to pass it and the legislature listened to them.

I have many times seen the need for such a law. We are able to work only in a limited way with the authority given under our general food law in protecting food from being kept too long in cold storage and we also are at a loss to know how much is in storage without the license provisions of cold storage plants.

The Massachusetts report quotes (8) a publication by Pennington (6) describing the condition of cold storage food in 1908:

Summing up the organoleptic properties, it may be said that for a short time, possibly six weeks or even longer, there is no perceptible change produced in a chicken by having it frozen. There certainly does not seem to be any evidence that it is better, and there is no convincing evidence that it is any worse. After three months, however, the fresh chicken is easily distinguished by its properties, as a rule, from the cold storage chicken, even after cooking, and to an absolute certainty before cooking. This distinction between the fresh and the stored bird becomes more and more marked as the time of storage increases .....

more marked as the time of storage increases ..... The general conclusion is, therefore, that in the case of frozen birds there is no indication of any improvement in quality—that is, in taste, odor, or flavor during cold storage. There is a deterioration which is noticeable, even at the end of three months, and becomes more marked as the time of storage grows longer. Hence, without any reference whatever to the question of whole someness, cold storage prolonged for six months or more appears to be distinctly detrimental as far as taste, flavor, and palatability are concerned.

Eleven years later Pennington testified before the House Committee on Agriculture of the 66th Congress (3). Evidently there had been vast improvements in cold storage conditions during that period as shown by her testimony which was in part as follows:

In the old days there was always a tendency to sell whatever was fresh, to hold it on the market until it was obvious that the market was not desirable, and then to put it into storage. You can see that, under such conditions, the goods going into storage were far from their pristine freshness. As the storage industry progressed, it was perfectly obvious to all storers that such practices were bad from the viewpoint of the reflexes of the practices themselves and also from the viewpoint of commercial success. Therefore, there came very quickly a tendency to put only high class fresh goods into storage, and that tendency has increased until it is now practically a habit. It is the exception, not the rule, these days for produce to go into storage which has been held on the curb pending a good market, which market did not arrive. And with the abolishing of that attitude has gone a great many undesirable phases so far as the palatability and desirability of the product is concerned. In fact, it has revolutionized the whole industry of the preservation of foodstuffs by cold.

Early in the investigations the Department (of Agriculture) published a brief outline of the conditions as it found them, the findings on the goods which were then in storage. From these analyses we drew certain conclusions which at that time were correct. I am very happy to say that that investigation, which is embodied in Department Bulletin No. 115, is now only of interest as a piece of past history. At that time we were perfectly right in saying that the goods ordinarily on the market from cold storage showed evidence of deterioration if it had been held for three months or thereabouts. I am very glad to say now that poultry can be held for nine months, the ordinary poultry as it goes in the storage warehouse in the ordinary channels of commerce with



Cold Storage Plant of the General Ice & Cold Storage Company, Inc., at New Bedford, Mass.

January, 1943

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Courtesy, Commonwealth Ice and Cold Storage Company Conveying Fish by Pan Elevators from Panning Room to Sharp Freezers

practically no deterioration, practically no change in palatability or in composition as determined by the most delicate tests that we can apply in the laboratory.

The Massachusetts document (7) stated that in 1911 California, Delaware, Indiana, New Jersey, and New York had cold storage laws. The Congressional document (1) stated that in 1919 cold storage laws (exclusive of those pertaining to the sale of cold storage eggs) were in effect in Alabama (licensing of warehouses only), California, Delaware, Illinois, Indiana, Iowa, Louisiana (by regulation by the State Board of Health under act of legislature), Maryland, Massachusetts, Nebraska, New Hampshire, New Jersey, New York, North Dakota, Ohio, Pennsylvania, Utah, and Wisconsin. According to the recent questionnaire the following states have cold storage laws, exclusive of those pertaining only to the sale of cold storage eggs: California, Delaware, Illinois, Indiana, Iowa, Louisiana, Maryland, Massachusetts, Nebraska, New Hampshire, New Jersey, New York, Ohio, Oregon, Pennsylvania, Utah, Virginia, and Wisconsin. Many of the states having no cold storage law nevertheless inspect the warehouses and the food contained therein under the general sanitary and food laws.

#### Summary of cold storage laws

Where there is a general law, its provisions require that the cold storage warehouses be licensed. The fees vary in some states in accordance with the amount of business carried on by the warehouses; in others there is a flat fee, irrespective of the amount of business, and in a few others, smaller fees for so-called locker plants.

As a rule, articles of food entering cold storage must be dated on receipt. In some but not all of these states, the article must be dated on removal from storage. Some states require the original dating on the package wherever the goods were stored. In one state an affidavit is accepted in lieu of a date upon the package. Most states permit storage for a period of 12 months. One state permits 9-month storage; one state permits 10-month storage with provisions for extension of time; and some states permit extensions after 12 months of storage. In three such states the annual report of the department must contain a record of each extension, together with the reason for granting it. In general, articles of food removed from storage for the purpose of being placed on sale cannot be again returned to storage, except that transfers in storage, not for the purpose of violating the law, are usually permitted.

Some states require that in retail stores the customer must be informed that cold storage food is for sale, usually by the display of a placard or poster. The law of one state requires that the customers must be so notified without specifying the method of notification.

The definitions of "articles of food" are somewhat variable. The favorite definition—for example, that of Massachusetts provides that "articles of food" include fresh meat, fresh meat products (except in process of manufacture), fresh food fish, poultry, eggs, and butter. That of New Hampshire has a similar definition except that the word "game" is added. That of New Jersey, in addition to the above articles, includes edible oils and fats. That of Delaware includes all articles of food except fruit and fish. Those of Iowa and Nebraska include all foods.

Thirty years ago there was considerable prejudice against cold storage food which, fortunately, is decreasing. A better quality of food now goes into storage and consequently is of good quality when sold. The comparatively new quickfreezing process has done much to remove public prejudice against cold storage foods.

Foods frozen by the above process are usually sold to the consumer in a frozen condition; and by applying the formula that the proof of the pudding is in the eating, he has ascertained that cold storage food can be of excellent quality and also be wholesome.



Figure 2. Maximum Holdings of Eggs and Poultry

Quotations from some of the replies by the state law enforcement officers who answered the questionnaire may be of interest.

Anton Roeger, Jr., of the Department of Agriculture of Pennsylvania, states:

You may be interested in knowing that the enforcement of the provisions of this law is one of the least troublesome of our problems and that, in general, we receive a rather high degree of cooperation.

Walter W. Schofield, New Jersey State Department of Health, writes:

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Figure 3. High Points in Cold Storage Holdings, 1917-25

It is our opinion that the operators of these warehouses do comply with the provisions of the law and that perishable foods are preserved at proper temperatures and other satisfactory conditions in these warehouses. We have found that there is a fine spirit of cooperation between these officials and this department in other details concerned with the enforcement, such as the marking of containers, and the filing of reports with this department

#### In 1928 I wrote as follows (4):

There are at present but few violations of the cold storage law. The owners of the warehouses comply with the act practically 100 per cent. A depositor may occasionally violate the law to a minor extent, but this is very unusual. Wholesale dealers in foods do not violate the law in dealing with their customers. A very few retail dealers violate in respect to the sale of cold storage eggs without the required label, but the great majority of such dealers sell cold storage eggs in cartons so labeled. Persons operating under the cold storage laws of Massachusetts are apparently of the opinion that laws are not made to be enforced but to be complied with.

So-called locker freezers have been introduced in recent years. They are fairly common in the producing areas but not so common in consuming areas. This type of freezer was not in existence when most of the cold storage laws were placed upon the books. A few states have amended their laws by making special provisions for such plants and relinquishing many of the requirements so necessary in public cold storage warehouses. The purpose of this type of storage is to enable the consumer to freeze articles of food which he himself has raised or purchased at wholesale and which he intends for consumption by himself and his family. There is but one such plant in Massachusetts.

Zean Gassmann, Illinois Department of Agriculture, writes as follows:

More than three hundred refrigerated locker plants are in operation in the State of Illinois, and we consider our law and regulations covering these an outstanding achievement inasmuch as the locker rooms must be equipped with recording thermometers and because it is the first time in Illinois that health examinations have been required for food handlers.

The Illinois law pertaining to refrigerated lockers is separate and distinct from the cold storage law, and locker plants are distinctly relieved of complying with certain sections of the general cold storage law. The following definitions are taken from the Illinois Refrigerated Locker Law:

"Locker" means the individual sections or compartments of a capacity of not to exceed 25 cubic feet in the locker room of a locker plant or branch locker plant.

exceed 25 cubic feet in the locker plant. "Locker Plant or branch locker plant. "Locker Plant" means a location or establishment in which space in individual lockers is rented to individuals for the storage of food at or below a temperature of 45 degrees above zero Fahrenheit and having a chill room, and sharp freezing facilities and facilities for cutting, preparing, wrapping and packaging meats and meat products, fruits and vegetables.

and meat products, fruits and vegetables. "Branch Locker Plant" means any location or establishment in which space in individual lockers is rented to individuals for the storage of food at or below a temperature of 45 degrees above zero Fahrenheit after preparation for storage at a central plant.

The law of New York state pertaining to refrigerated warehouses and locker plants contains the following definition:

The term "locker plant" shall mean any building or portion thereof, under refrigeration, in which individual compartments,

each of not more than 12 cubic feet capacity, are rented to individuals for the sole purpose of the storage and/or freezing of privately owned articles of food for use and consumption by the owner of the food or by his family.

That law also exempts locker plants from the operation of several sections of the general cold storage law. If these locker plants are found to be successful, they undoubtedly will increase in number in the United States.



Figure 4. High Points in Cold Storage Holdings, 1938–42

January, 1943

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Courtesy, Commonwealth Ice and Cold Storage Company Storage Room for Frozen Fish, Showing Swordfish in the Aisle

The next step following the development of the locker plant would naturally be a cold storage warehouse in the home. It is here. An interesting account of this innovation was given recently by Sparkes (9).

#### Statistics

Many of the state laws, including that of Massachusetts, require a report to the enforcing department of the amounts of food held in storage. These figures were of news value fifteen years ago, and may again be useful for that purpose. At that time the Massachusetts newspapers would ask for the quantity of food in cold storage and would play up the figures as being enormous when, in fact, they were almost insignificant. This attitude on the part of the press was circumvented by giving the per capita holdings as well as the total holdings. Statements to the effect that there was in cold storage for each person, two thirds of an egg, seven hundredths ounce of lamb, one quarter pound of pork, etc., invariably carried as much prominence in the paper as did the actual figures, which were the above figures multiplied by four million.

In the early days of the last war the Massachusetts Food Administrator made inquiries of the department relative to the Massachusetts reports of holdings in cold storage; but the Administrator required and obtained additional and more voluminous reports of food holdings than the Department of Health possessed at that time. The United States Food Administration then collected statistics as to holdings of food, not only in cold storage warehouses, but elsewhere. At the close of the war the continuation of this statistical work was taken over by the United States Department of Agriculture and is now maintained by the Agricultural Marketing Administration of that department.

Each month valuable statistical information is compiled pertaining to frozen fruits and vegetables, dairy and poultry products, frozen and cured meats. These reports are available to all citizens provided they are of value to such persons. The data from which the charts were made came from these reports.

There is a seasonal variation in the production of food. The surplus in times of excessive production goes into storage for release in times of scarcity. H. C. Marshall estimated that not more than 10 per cent of our perishable foods is placed in cold storage (2).

Figure 1 gives the per cent of maximum holdings based upon the five-year averages from 1935 to 1939. The maximum and minimum holdings of the various items occur in the following months:

Item	MAX. HOLDING	MIN. HOLDING
Poultry	Jan.	July, Aug.
Pork	March	Nov.
Lamb	Jan.	Aug.
Beef	March	July
Butter	September	April
Cheese	Oct.	March

Figure 2 shows the monthly percentages of maximum holdings of "shell" eggs and of fowl and "roasters". When the surplus fowl goes on strike and declines to produce eggs, her owner places her in cold storage, to the enhancement of his exchequer. But when the hen is producing surplus eggs, she is cod

too valuable for food.

Figure 3 shows the maximum holdings per year of beef, pork, lamb, butter, cheese, and poultry in the United States from 1917 to 1925. In 1921 there was a tremendous increase in the storage of lamb due to the importation of New Zealand lamb, much of which was stored on the East Coast. The first few shipments were sold at retail but the balance eventually went to England where it belonged. An inquiry made of the manager of one of the large packing houses resulted in a statement that the United States sheep growers informed the packers that if they wished New Zealand to raise their sheep, the United States sheep raisers might as well quit.

From 1918 to 1924 beef as well as lamb showed a proportional drop except for the enormous increase in lamb due to importation from New Zealand. The monthly holdings of lamb are plotted on Figure 3 from January, 1920, to July, 1921. There are two maximum figures for 1920, the normal figure in January as well as the excessive figure due to New Zealand lamb.

In 1920 the Massachusetts Department of Public Health granted extensions of storage time for 216,688 pounds of beef and 5,502,152 pounds of pork. In 1921 similar extensions were granted upon 937,433 pounds of pork. Regarding the extensions in 1921, the Annual Report states: "This pork was practically all export pork, being cuts not sold in this country, and held in Massachusetts pending foreign shipment which was delayed by certain import embargoes imposed by the countries to which the material was to be shipped." Comparing these extension figures with those of 1940 (beef extensions 19,288 pounds and pork extensions 62,084 pounds), it is evident that the holdings of beef and pork, at least in Massachusetts cold storage warehouses during 1920 and 1921, were somewhat excessive.

From 1918 to 1921 butter and poultry showed the same proportional decrease in holdings as did beef and lamb, but after that interval the importation of Danish butter and Czecho-



Engine Room in the Plant of the Commonwealth Ice and Cold Storage Company

slovakian poultry were to some extent responsible for subsequent increases in holdings.

Figure 4 shows the maximum holdings from 1938 to 1942 of pork, butter, cheese, poultry, beef, eggs, lamb, and mutton in the United States. The slanting lines are parallel, and the data points show substantially the same proportional increase in storage holdings of each article.

Figure 5 shows the holdings in pounds of butter and cheese, in cases of shell eggs, and in case equivalents of frozen brokenout eggs. The shell eggs naturally show a greater seasonal variation than do the broken-out eggs. The shell eggs are practically all removed from each warehouse by February 1, whereas broken-out eggs are held in storage all the year because they are kept in a frozen condition and deterioration is prevented. Butter and cheese show similar trends each year, but the variation in the cheese figures is less than that for butter. Very little butter is held in storage for a year; its inherently fine quality is due to its freshness, which is not true of cheese.

Figure 6 shows the seasonal variation in the holdings of meats. The holdings of cured pork are invariably in excess of those of fresh pork; but the holdings of fresh beef are much in excess of those of cured beef or of beef in the process of curing. We eat considerably more hams, smoked shoulder, and bacon than we do of cured beef.

Hams and bacon in the so-called old days were cured with a view to preservation only. Today hams and bacon are lightly cured principally with a view to flavor. Meat intended for curing is now kept in cold storage until such time as it is needed for processing, and thus the quantity of mildly cured meats offered for sale to the consumer is not so excessive that it cannot be consumed before spoiling.

The holdings of lamb and mutton do not show the extensive seasonal variation as do beef and pork.

Figure 6 also shows the poultry holdings. Poultry is classified by the United States Department of Agriculture into seven groups—broilers, fryers, roasters, fowl, turkeys, ducks, and miscellaneous. It was impossible to make a comprehensive chart because of overlapping lines; because of similarity in seasonal variation, the broilers and fryers were grouped together, as were the fowl and roasters. The figures relating to miscellaneous poultry were not plotted.

The storage of ducks begins in June and reaches a maximum in September or October. In August the broilers and fryers are next stored, reaching the maximum in January. The fowl and roaster storage begins in October, reaching the maximum in January; and turkey storage begins in December and reaches the maximum in February. Much of the storage poultry is used by hotels and restaurants; a smaller but not inconsiderable quantity is sold direct to the consumer.

The storage of frozen fruits and vegetables as pounds and of apples (not frozen) as bushels is also shown on Figure 6. There are no statistics of holdings of apples between July and September, although frozen fruits and vegetables are kept in storage the entire year. These statistics of fruits and vegetables are an innovation established only a few years ago.

The frozen fruits and vegetables upon which statistical reports are published are segregated as follows:

FRUITS, FROZEN	VEGETABLES, FROZEN
Blackberries	Asparagus
Blueberries	Beans, lima
Cherries	Beans, snap
Young and similar berries	Broccoli, green
Raspberries	Corn, sweet
Strawberries	Peas. green
Other fruits	Spinach
Classification not reported	Other vegetables
	Classification not reported

In addition, the figures are further segregated in the case of frozen fruits into those stored in containers of less than 30pound capacity and those stored in bulk or containers exceeding 30 pounds.

#### Length of time in storage

Inquiries are often made regarding the length of time food is kept in storage. It is unprofitable to store it beyond the beginning of the time of surplus production because of the drop in price and the storage charges. For these reasons the bulk of this food is removed after six months, and after nine months the depositor faces a loss unless the food can be held over until the next season. This is the reason for the extension provision in the law. Unforeseen conditions have a bearing upon such requests. For example, a few winters ago there was an extraordinary off-season run of mackerel at the time when storage mackerel was due to be removed for retail sale.

Extensions of time in cold storage in Massachusetts are granted for an average period of three to four months. In 1941, exclusive of eggs in the shell, 240,077,270 pounds of food were placed in cold storage, and during that year extensions were granted upon 732,025 pounds, representing 3.04 per cent of the food subject to such extension. Requests are never made for extension of storage time for shell eggs.

#### **Public health aspects**

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Formerly it was embarrassing to a health department official enforcing a cold storage law to be asked what value, if any, cold storage was to the public health. There is a satisfactory answer now—namely, the destruction of parasitic infections in meat which cannot be detected by ordinary inspection.

TULAREMIA. Massachusetts is unusually free from tularemia, also known as deer fly fever. To prevent its introduction, the Massachusetts Department of Public Health in 1929, under the provisions of a statute passed that year, adopted a regulation requiring that carcasses of rabbits shipped from other states into Massachusetts must have been kept in cold storage at a temperature of less than 30° F. for a period of not less than 30 days. This regulation is rigidly complied with. The wild rabbits in Massachusetts are free from the disease, and the Department of Conservation has a regulation requiring quarantining of imported live rabbits before they are liberated.

TRICHINOSIS. This parasitic infection can also be controlled by cold storage. Freezing for a sufficient time will kill the trichinae which are so prevalent in pork. No system of inspection can guarantee pork to be free from this parasite; consequently one must always assume that pork is diseased. The remedy is to cook it to or beyond the point where the red color is entirely destroyed. Certain races prefer to eat undercooked pork, and trichinosis in humans is usually confined to these people. The disease is probably more prevalent in humans than the records show, because of the liability of an incorrect diagnosis.

The United States Bureau of Animal Industry has regulations pertaining to the preparation of meat products intended to be eaten without being cooked. Freezing is included among them. In 1924 the Massachusetts Department of Public Health adopted certain regulations based upon the federal regulations, one of which reads as follows:

If refrigeration is employed, the pork shall have been subjected to refrigeration not less than twenty days at a temperature not higher than 5° Fahrenheit, provided, however, that pork does not exceed one hundred pounds weight per package. If in barrels or tierces, the pork shall have been subjected to refrigeration not less than thirty days at a temperature not higher than 5° Fahrenheit.

At the time these proposed regulations were being considered for presentation to the Department, the late Francis X. Mahoney, then Commissioner of Health of the City of Boston, stated in substance: "If it is true that freezing will kill trichinae, I believe that there should be a law on the books requiring all pork to be frozen prior to being placed on sale."



Figure 5. Cold Storage of Butter, Cheese, and Eggs

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Other departments are giving serious attention to this subject as shown by a letter received from Walter W. Schofield, New Jersey Department of Public Health, stating in part:

I would like to direct your attention to additional regulations which this Department has under consideration at this time concerning the certification of the refrigeration of pork by operators of cold storage warehouses. This matter was brought to our attention by the Department of Health of New York City, which Department requested the adoption by this Department of regulations governing the certification of pork stored in warehouses of New Jersey, but which is to be marketed in New York City. The holding of pork at low temperatures for the time specified in the regulations would destroy trichinae and the certification of this storage, plus the marking of containers of such products with a statement of the temperature and time of storage, would enable buyers to purchase pork which had been properly refrigerated for the destruction of trichinae. It is my opinion that this proposal has considerable merit. Of course, it may take a considerable period of time to inform the public at large of this additional safeguard in this particular matter.

The regulations were adopted in July, 1942, one of which is as follows:

The temperatures and periods of time necessary for the destruction of trichinae shall be based upon the size of the pieces or packages of pork. Pork in group 1 shall consist of pieces not exceeding six inches in depth, or stored as solidly frozen blocks not exceeding six inches in thickness. Pork in group 2 shall consist of pieces or layers or contents of barrels or containers, the thickness of which exceeds six inches, but is not in excess of twenty-seven inches. Pork in group 1 and group 2 to be refrigerated for the destruction of trichinae shall be subjected to a temperature of  $5^{\circ}$  F., or minus 10° F. or minus 20° F. for not less than the corresponding number of successive days, as indicated in the following table:

Femperature	Group 1	Group 2
5° F.	20 days	30 days 20
-20	6	12

The regulations also provide for a certification to be attached to each lot so frozen.

The state of New York now has in effect a regulation some-



Courtesy, Commonwealth Ice and Cold Storage Company Storage for Frozen Fish, Showing a Section of Bins Used for Small Lots

what similar to that of New Jersey. If the New Jersey and the New York regulations remain in effect, an interesting experiment is underway, and its public health significance as determined by epidemiological studies will be of value, both to public health authorities as well as to the trade. The success of this experiment, however, must depend upon the education of those persons who prefer to eat rare rather than welldone pork.

#### Cold storage as a war measure

During the last war the United States fed many millions of people in England, Belgium, and France. During the present war we are feeding millions in England and Russia. During the last war there was considerable expansion of the cold storage business. Warehouses which had been closed were reopened. In Massachusetts several new warehouses were built, mostly for the freezing of fish to be shipped abroad and to be shipped west to conserve meat. Increased storage space was necessary for temporary storage of meat to be shipped abroad. The increased production of fish, pork, and beef required increased storage space. The war ended in November, 1918, and after a few years we had, at least in Massachusetts, a surplus of cold storage warehouses. Many of them have been torn down, sold at auction, or are not now in operation.

Will history repeat itself? The Agricultural Marketing Service of the United States Department of Agriculture is becoming interested in warehouse space. The following is quoted from a report of that service issued September 20, 1941:

The gross space in all cold storage warehouses and meat packing plants in mid-June of this year totaled 764,646,000 cubic feet according to a preliminary report issued today by the United States Department of Agriculture. The report is based on a survey of refrigerated warehouses and meat packing establishments made by the Department's Marketing Service at the request of the Transportation Division of the National Defense Advisory Commission.

The refrigerated warehouse space existing this year indicates that over the 21-year period from 1921 to 1941 a net expansion of 221 million gross cubic feet has occurred in all types of plants. The trend has been generally upward during this entire period, the major exceptions being the years 1933 and 1935 when some abandonment of obsolete warehouse space occurred. Since the biennial survey of 1939 there has been a net increase of all types of plants totaling 18.2 million cubic feet.

The monthly reports of that service now carry the percentage of cold storage space occupied in public freezers. Probably there will soon be a demand for cold storage space in excess of that now available, and one can but wonder if capital will be willing to take another chance, even though this may be essential for the conduct of the war.

## Variation in composition due to cold storage

There are certain possible changes which may occur in food held in cold storage. First comes evaporation, because the atmosphere is practically dry due to the freezing of any moisture in the air. Consequently frozen foods, unless properly protected, are liable to lose moisture. If desiccated to any great extent, the sale value is lessened. Certain enzymes do not lose their activity at freezing temperatures, and enzyme action is to some extent responsible for changes in cold storage. Lipase activity is responsible for increased rancidity in storage butter. Butter infected with mold so slightly that it is not visibly apparent at the time of storage will sometimes exhibit considerable mold when removed. Eggs in the shell are kept above the freezing temperature, because if frozen. the yolks will coagulate. Storage eggs are subject to the same changes but to a lesser degree than those stored at a higher temperature. The changes are loss of moisture, increase in the acid number of the fat, increase in ammonia in the yolks, and decrease in dextrose.

Times are changing, but in many respects history is unfortunately repeating itself. Pennington's statements of 1908 may again be the rule and not the exception.

At present the rendering value of bad meat is considerably less than its value as raw material for the manufacture of sausage. The Massachusetts inspectors are now finding and confiscating more bad beef and pork trimmings in cold storage warehouses than during many prior years. They are also finding and confiscating much bad meat in sausage factories; in one instance they made a confiscation in a sausage factory operating under federal inspection.

The cold storage process is not responsible for these conditions, and it is hardly to be expected that warehouse employees will investigate the condition of each barrel of meat

trimmings submitted for storage. If the meat is obviously bad, the warehouse should and frequently does decline to receive it; but if it is of doubtful quality, the warehouse record may contain a statement to that effect, after which the state inspector is liable to find the record, as well as the meat, and ship the meat to the rendering plant.

The question is often asked, "Why does meat get into such condition?" The answer is, "The meat has been held too long unrefrigerated, with the expectation of a rise in price and then is sold for manufacture into sausages." These criticisms, however, are as yet the exceptions.

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# Canning technology

E. J. CAMERON, National Canners Association, Washington, D. C.

• • • Developments in canning technology are in the stage of rapid transition, and to a notable extent they have taken a course parallel to changes in the manufacture of containers.

In guiding the course of the tin conservation program, the laboratories in the can manufacturing and canning industries have been investigating substitutes for hotdipped tin plate. Bonderized (or pretreated) steel and electrolytic tin plate give most promise as substitute materials and are coming into increasing use. Information obtained on the applicability of the new containers is being applied as facilities are expanded for manufacture of the new materials. New containers are being studied from the standpoint of susceptibility to external and internal corrosion.

The development and use of substitute solders which are low or lacking in tin and correspondingly high in lead is of technical importance in canning, and investigations are now underway to test suitability from manufacturing and public health standpoints.

IN TIMES like the present, no paper attempting to review recent developments in canning technology would be worth-while without emphasis on the subject of canned food containers; and I do not believe I would have had the courage to prepare such a paper had it been scheduled in advance of the June meeting of the Institute of Food Technologists. It was then that Lueck (6) presented his comprehensive interpretation of the metal container situation which has become "must" reading for canning technologists. His presentation and a previous one by Lippert (5) have been outstanding in resolving a great amount of speculative and disorganized thinking into terms of intelligible analysis.

Canning technology is in a stage of rapid transition from the standpoint of containers and for other reasons. Many

changes have already occurred, and others will take place during the war period. Some of them will be temporary, and others will probably become permanent. It is a safe prediction that canning practices of the postwar period will carry the mark of wartime experience and development.

The container problem calls for first consideration, and the rapid sequence of changes in thoughts on the subject are associated intimately with orders and requests from the OPM, later the WPB, and other governmental agencies. Orders M-81, M-81-a, M-81 revised, M-118, M-126, and others of the War Production Board are now familiar documents. The "81" orders have been directed particularly to the restriction of tin usage. M-118 is in the interest of rubber conservation. M-126 relates to conservation of iron

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Feeder End of Installation Built by Wean Engineering Company for Bonderizing Black Plate

and steel. Now interest attaches to the steel problem, and consideration is being given to the alternate or required use of glass in place of metal containers.

The basis for the container changes which have been ordered is not to be found in the discussions of the OPM days. The background lies in the work which was done much earlier in the laboratories of the can manufacturers. It is questionable whether anyone can say definitely just when work on substitute containers began, but some work on black iron containers was underway in the early twenties. Also, the Quartermaster Corps had an interest in some experimental packs in black iron cans which were being studied by this laboratory, and the interest was not in tin conservation but in the avoidance of glare which might result from the reflection of sunlight from bright tin plate.

One of the first conferences, if not the first, to consider ways and means of conserving tin and of arriving at an effective reduction in its use for metal containers was called by the chief of the conservation unit of the Office of Production Management in April, 1941. The principal subjects for discussion were:

1. Nonessential civilian uses of tin can containers, curtailment of which might be effected with minimum hardship in the event of a shortage of tin.

2. Possibility of developing substitutes that could be used for such purposes.

3. Possible effect of reducing to various percentages the amount of tin coating on containers.

The conference amounted chiefly to an exploration of the means of effecting reduction in tin consumption; but no definite proposals were made, and the meeting adjourned on the note that the can manufacturing industry would make reasonable changes where practicable and would hold itself in readiness to make still further changes if necessary. The net result was a prompt reduction of 10 per cent tin coating (from 1.50 to 1.35 pounds per base box pot yield) for cans to be used for packing a majority of processed canned products, but excluding certain so-called class 1 products (kraut, pigmented fruits, and other products of corrosive character). Further savings were effected by the reduction or complete prohibition of the use of tin for containers used in packaging nonprocessed foods. These reductions were progressive until Order M-81 became operative nine or ten months later. Then a limit of 1.25 pounds per base box was set for containers for most of the processed products that were allowed to be packed. This amounted to a reduction of about 17 per cent from the original weight.

#### **Reduction in tin content**

The requirement in M-81 had to have some experimental basis, and its genesis was in a so-called tin-conservation pack which was put up in the fall of 1940 to test the effect of the extreme reduction in tin coating of from 1.50 to 1.25 pounds. In the main, this represented a coordination of the work already underway in the laboratories of can manufacturers and was a collaborative venture. The can manufacturers supplied the containers and most of the products, and the National Canners Association conducted the tests. Colonel Paul P. Logan, Quartermaster Corps, who was one of the first to see the need of tin conservation, played a leading part in planning the program.

The test cans and control cans were packed with various food products selected to represent major classes with reference to their action on tin plate. Twelve typical food products were canned, representing fruits, vegetables, fish, milk, and army rations. Among these products were foods which would be expected to produce varying degrees of corrosion, perforation, hydrogen springer formation, and iron and tin discoloration. Packs were incubated at 85° F., a storage temperature which would reasonably accelerate any abnormalities that might occur by reason of the lighter tin coating without producing such false effects as might result at a substantially higher temperature. Periodic cuttings and examinations were made over an 18-month period, the examinations including organoleptic observations, visual examination of the cans for evidence of corrosion or discoloration, and chemical tests of the contents for tin and iron.



Conriesy, American Can Company

In the report on the 18-month cutting, the following conclusions were drawn:

1. Cans manufactured from 1.25 hot-dipped tin plate are satisfactory containers for such products as peaches, tomatoes, peas, army rations (M-1, M-2, M-3), spinach, shrimp, and evaporated milk.

2. The use of 1.25 plate in place of 1.50 plate will result in early corrosion losses in certain of the more corrosive products such as canned dried prunes, apricot jam, and RSP cherries.

This short summary should be supplemented with the statement that where corrosion occurred in the 1.25 plate, it was found later or to a lesser extent in the control plate. The report should not be taken to establish that in all respects, even in the case of the noncorrosive products, the lower weight was as satisfactory as the higher. It is known from commercial experience that some extra care has been necessary in the handling of the 1.25 containers to prevent external corrosion.

#### Substitute cans

One of the most intense activities in the industry at present is the investigation of the so-called substitute cans and substitute solders, the latter also being in the direction of tin conservation. Lueck (6) gave a full description of the metallic substitutes. Coordinated work on this subject is being pushed as rapidly as can be done intelligently. The individual can manufacturers are making their own tests and investigating the variables which each considers to be most significant. This laboratory is following the work of each, and in addition has made a selection of such experimental packs as appear most promising in representative groups of fruit, vegetable, marine, and meat products, and evaporated milk.

A number of variables is involved in these packs. Electrolytic plate, for example, is prepared by electrolysis from either an acid stannous sulfate or alkaline sodium stannate bath. Exploratory packs indicate that a different service value may be expected, at least with some products. The type of finish produced on electrolytic plate may be varied,

the melted (fused or flow-brightened) finish apparently being superior. Electrolytic plate for the packs which we are studying carry 0.5 pound of tin per base box, with the exception of two lots where 0.1 pound is used. The matter of appropriate enamels on the inside of the can is much more important than when hot-dipped tin plate is used; and what enamels may be used and under what circumstances will have to be worked out by the industry. The experimental packs already put up and now being prepared will test the enamel problem in a comprehensive way. Bonderized plate must be enameled, and the electrolytic plate will have to be enameled for use with a good many products for which an unenameled 1.25 plate would prove satisfactory. With the advent of the new containers there will obviously be production and equipment problems which must be met by the manufacturers.

In furtherance of the program of tin conservation, the War Production Board, on June 13, issued Supplementary Order

M-81-a covering the use of tin plate and black plate for cans of designated products. For one group of products the order required that a specified proportion of the cans have ends with a tin coating not in excess of 0.50 pound per base box if the can has a soldered side seam, and have both ends and bodies with a tin coating not in excess of 0.50 pound if the side seam is not soldered. For another group, phosphated black plate (Bonderized plate) is required for the ends of can with soldered side seams, and for both ends and bodies of cans without soldered side seams. For a third group, ends or complete cans, depending upon whether or not the side seam is soldered, are required to be made of either phosphated black plate or tin plate having a coating not in excess of 0.50 pound.

Manufacturing facilities are nowhere near adequate to supply the Bonderized plate and electrolytic plate necessary for complete execution of this order at this time. Perhaps this is a fortunate situation. If manufacturing facilities were adequate, there would be danger of the use of these materials far beyond our knowledge of their applicability. At present, through the partial use of these substitutes in commercial packs, we are undertaking a large industrial experiment, and from this point the increase in information on the use of substitutes and the increase in facilities for their manufacture will probably run more or less parallel courses.

That the introduction of the new containers would affect canning procedure has been anticipated, and the subject is well covered in a publication of the Can Manufacturers Institute (3). This bulletin sets forth a number of recommended practices, many of which reiterate advice in regard to the proper handling of the conventional tin can, but some of which have more specific reference to the new containers. Attention is called to corrosion attributable both to canning practice and to storage conditions. Both external and internal corrosion are discussed in a practical way.

#### Substitute solders

Lueck (6) discussed manufacturing experience with lowtin or "tinless" solder. He pointed out that the lead-silver

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solder with the original composition 97.5 per cent lead-2.5 per cent silver is being used commercially for containers made of hot-dipped plate and electrolytic plate, but not Bonderized plate. Unsatisfactory experience with the last is due to the fact that the solder does not alloy readily with the steel. Experience showed further that, when the lead-silver solder is used, tin is picked up from the cans and the composition of the solder bath reaches an equilibrium at approximately 2 per cent silver-5.5 per cent tin-92.5 per cent lead.

The question has been raised as to whether, when the highlead solder is used, we may expect a greater lead pickup in the food than would be expected with the 40 per cent tin-60 per cent lead alloy. In the conventional "sanitary" type of can little, if any, solder is exposed to the can contents except on rare occasions when the solder is excessively sweated through the seams. In the case of the floated-end type of can a small area of solder is always in contact with the can contents. Commercial experience over many years and experimental evidence have shown that the lead pickup from the 40-60 solder is so small as to cause no concern.

The relative degrees of lead pickup from the 40-60 solder, the lead-silver solder, and lead-silver solder with two levels of tin (2.5 and 5 per cent) are being studied here. The method is empirical and constitutes an exaggerated test in that a relatively large area of solder coated on a tin disk is brought into contact with the test food in a deleaded glass jar which is subsequently sealed, processed, and held in storage at 98° F. The test foods are evaporated milk, orange juice, chopped green beans, and corned beef hamburger. Early results indicate that on the basis of maximum expected exposure the difference in lead pickup is not significant.

Supplementing the study of the solubility of lead from solder in different foods, an elaborate series of feeding tests



Relative Bonding Strengths of Reduced Tin-Content Solders at 250°F. Courtesy, American Can Company

is being made at Yale University, under George R. Cowgill's direction; pellets of the lead-silver solder, alone and with two levels of tin, are being fed to rats in exaggerated amounts. This obviously is a public health investigation, and is a continuation of a study which has been underway at Yale for over two years on the effect of ingestion of metallic solder of 40 per cent tin-60 per cent lead composition. In the first study both rats and dogs were used as test animals, and lead pickup by the animals was essentially negative.

#### **Glass** containers

Glass containers have been referred to frequently as substitute containers. This follows a fairly general misconception that only foods which are processed in metal containers are "canned" foods. That is not the case at all, and glass containers have been established in their own right in modern canning. Glass, then, provides the material for alternate, rather than substitute, containers for heat-processed foods. In 1941 fruits and vegetables packed in glass amounted to 14,000,000 cases, or about 4 per cent of the total. For 1942 it is estimated that the glass pack will reach 31,000,000 cases, or 11 per cent of the total. In this connection, however, it must be emphasized that under Conservation Order M-119, issued in the interest of rubber conservation, there cannot be any substantial turning to the use of glass for products for which tin is prohibited under Order M-81. As a practical matter the situation seems to have resolved itself into determining, first, what foods should be permitted as heat-processed products in either metal or glass containers and, secondly, what the proper balance is between the two, considering the necessity for conserving both tin and rubber.

From the standpoint of canning technology a change-over from one type of container to another calls for material changes in operation. Not only is an equipment problem involved, but the usual procedures must be adjusted to meet the change. In particular, exhausting, processing, and cooling methods must be revised and additional equipment provided.

Through editorial columns and elsewhere, much has been said about the possibility of plastic, fiber, or other nonmetal or nonglass containers as substitutes for the conventional containers; but nothing has yet come to light which suggests the utility of such substitutes for heat-processed foods. This is not to say that the eyes of canning technologists are closed to such a possibility, but those who have had experience in testing even minor changes in containers know that should a plastic or fiber container be produced which theoretically and experimentally appears to fulfill all the requirements of an efficient container, much time-consuming work will be necessary to get the "bugs" out of it. However, should a promising substitute come to view, the best technological talent in the industry will give major attention to its proper testing.

#### **Canning methods**

Everyone who has given thought to the subject recognizes the effect on canning practice of the rapidly changing container situation. However, few have realized the extent to which the various Conservation Orders have influenced canning methods. This has been especially true in regard to formulation of products, but not entirely so. The motivation of such restrictions and requirements has been to make optimum use of the container materials which are available. Without attempting to cover this point exhaustively, I wish to cite a few examples.

Under the original Order M-81, dried products were excluded, not only as such but in combination with the canning of fresh vegetables. Potatoes were excluded. Thus, there was prohibition against the packing of mixed vegetables using potatoes or dried products such as lima beans or peas. It is my understanding that no processed vegetables may be used in any mixture of vegetables and, for purposes of definition, frozen vegetables are held to be processed. This would prohibit also the canning of the mixture of such a popular product as carrots and peas if either ingredient had been either canned or frozen. It has even been suggested that the cold storage of vegetables constitutes processing, although it would appear that this extension of the definition would be difficult to justify.

It is well known that ready-to-serve soups have, by order, been displaced by condensed soups. The background of this change is Order M-81, and the amendment, issued in April, sets forth what kinds of soups may be packed and specifies the lower limit of dry solids which would apply to each kind. M-81-a, as amended in June, went further and stipulated minimum solids, or gravity, for certain tomato products, notably in the case of pulp or purée, the specification for which was lifted from 8.7 per cent salt-free solids (as provided in the standard of identity) to 10.7 per cent. Other examples could be cited and all of them to a greater or lesser degree influence plant practice.

A notable example of voluntary action on the part of one branch of the industry to coordinate its policy with the conservation program occurred when the shrimp canners, as an industry, suggested it be made mandatory that the drained weight of canned shrimp in the can be increased substantially. This desire was made legally effective after the usual hearing by an order issued by the Federal Security Agency, which fixed the weights at certain minimums according to size of can and style of pack.

#### **Peacetime problems**

For the better part of 1942, in scientific meetings the references to changes in food production and handling, and in fact to other technical matters, have been associated largely with the war situation. This carries the suggestion that almost everything in the nature of development just prior to the outbreak of hostilities was in anticipation of the emergency, and that when war came most work stopped except that which was directly tied to the prosecution of the war. Perhaps that is the way it should be, but there has been every reason to carry on to a reasonable conclusion some of the more promising lines of work which were well under way when war was considered by many of us to be a fairly remote possibility.

One of the recent advances in canning technology not associated with the war has been the definition of practicable methods to stabilize to a high degree the chlorophyll of green vegetables such as peas. One method has recently been the subject of a hearing before the Food and Drug Administration on a petition to amend the standard of identity for canned peas to include peas which had been subjected to the stabilization treatment. The hearing covered a period of several days, during which there was a thorough exploration, under quasi court procedure, of all the important technological details and many minor ones. To state the matter briefly, the stabilization of the green color by the method is the result of the adjustment and control of pH by treatment with small quantities of harmless alkaline reagents. This control results in the maintenance of green color by preventing, substantially, the dissociation of magnesium from the chlorophyll molecule. Peas so treated have been canned to a commercial extent. The method of stabilization lacks perfection and work toward that end remains to be done. Further investigation of the problem must wait until we can give renewed attention to peacetime matters, but a noteworthy advance has been achieved.

Another peacetime development which under other circumstances would receive far more attention than is given here, is the increasing application on a commercial scale of the principle of high temperature-short time sterilization, or pasteurization, of canned fruit and vegetable juices. The principle is almost universally employed in the canning of citrus juices and has come into wide use with the vegetable juices. The development follows the direct or implied prophecy made by Ball (2) before the 1937 Food Technology Conference at M. I. T. At the same conference Ayers (1) discussed flash pasteurization of fruit juices. The principle as applied to canned vegetables is just as sound as it is in the case of acid products, but very high temperatures are necessary for short-time sterilization of vegetables, and the application calls for further experimental work requiring specialized equipment. Consequently such work cannot be undertaken during the war.

#### **Dietary research**

There is much activity in the field of nutrition, and practically all of it dates back to the President's Conference on Nutrition in May, 1941. Present studies on the nutrition of canned foods in a sense date to that conference, but it is not the initial undertaking. For more than fifteen years the canning industry supported work of this nature at Columbia University, as evidenced by the many reports by W. H. Eddy and E. F. Kohman on the vitamin content of canned products, reviewed in a recent bulletin (4). This work terminated in 1937, and since that time there has been a great accumulation of new knowledge, especially on the B vitamins and methods of assay. As the matter stands now, the industry is awake to the necessity for extending its knowledge on the protective factors.

The first phase of the program contemplates the assay of about twenty-five canned foods, including fruits, vegetables, and sea foods, for six vitamin factors (A, C, thiamin, riboflavin, niacin, and pantothenic acid) which are of recognized importance in nutrition. Assays will be made also for important minerals. The products to be studied will be taken from all parts of important sections in which they are canned. It is expected that about thirty thousand samples will be taken during the course of this year's program. Certain collaborative studies will be included, and grants have been or will be placed with five universities.

This part of the work is directed to the acquisition of much needed information on what canned foods contain beyond the basic nutrients. For the first year's study, the decision to give almost exclusive attention to taking a census of dietary factors in canned foods was inspired to a great extent by repeated calls for such information by purchasing authorities in the armed services and elsewhere.

Leading from the first phase of the investigation, technological research will be undertaken to show the way to better retention of the dietary factors in products where there is an indication of reduction as the result of the canning procedure. As we look on the matter now, the possible ramifications of this line of study are almost limitless. Field and factory research will be necessary, and chemistry will be tied with engineering in reaching the objectives. But before embarking upon such technological investigation, we must have the basic information which we are now attempting to obtain.

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# Packaging trends

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The packaging trend with respect to Conservation Orders of WPB is discussed. Illustrations are given in the transfer of foods, medicinals, and chemicals from one type of container to another, with attending advantages or disadvantages. The lightening of the weight of metal used in containers and caps is discussed, together with reference to size and shape of containers. The manufacture of electrotin plate is illustrated.

TN PACKAGING we may classify containers under four headings when they are considered from the standpoint of material construction of the body of the container, or the wrap of the package. These groups are cellulose, metal, glass, and plastic resin. Each one of these groups will have four or more important divisions, and many minor subdivisions. For example, cellulose would include wood, cardboard, paper, and fiber. Metal would include tin plate, terne plate, steel plate, Bonderized plate, zinc, and galvanized sheet. Glass would include bottle glass, opal glass, stoneware, and porcelain. Plastic resin would include Bakelite, ureaformaldehyde, lignin, and polyvinyl acetals.

The closure for a package is often made of a material from a group entirely unlike that of the body of a container—for example, a metal closure for a glass jar or metal ends for a paper canister. Keeping the above classification in mind, it will be evident that hundreds of combinations and substitutions are possible simply through interchange of the component parts of a container, without even taking into account any of the many subdivisions. It is just this fact that is now influencing the packaging trends during the present emergency. The packaging trends are, of course, primarily influenced by the relative availability of the materials used in construction of containers.

However, other extremely important considerations enter into the picture of the present trend in packaging: (a) the nature of the end product to reach the consumer, (b) the weight

#### A. H. WARTH, Crown Cork & Seal Company, Baltimore, Md.

and size of the container or of its component parts, (c) the type of equipment required and its availability, (d) the stability and appearance of the product necessary to receive consumer acceptance, (e) the proofness of the package against poisonous gases when shipped to an area of combat, (f) the speed of filling and the amount of labor involved in packaging, (g) the cost in relation to the price ceiling already established for the material packaged.

#### **Shortages**

The packaging trend within the past year has been almost entirely influenced by either Conservation Orders of the War Production Board or their contemplation through known shortages of materials needed for the armed forces. Aluminum was one of the first materials to be replaced. For example, aluminum and other metal barrels were used by brewers in delivering beer to taprooms where the beer was



#### Looking Down the Top of the Tin-Plating Tank

The strip enters, then passes over and under rolls spaced about 12 feet apart vertically. This tank is made up of sixteen passes, or thirty-two vertical strands, between each of which is a one-ton anode. Each top roll carries power.

dispensed by the high-pressure system to the consumer. The metal barrel is being replaced by white oak properly reinforced. The latter has been named the "high-pressure victory barrel" by the Blatz Company of Milwaukee (1).

A large tonnage of aluminum foil had been used to face the composition cork disks in bottle caps sold for sealing malt beverages. Almost a million pounds of aluminum foil were so used by the bottle cap manufacturers. This foil has been replaced by varnish-coated paper spot materials. Foils were extensively used in wrapping chocolate buds and bars and wrapping cheese. They have been largely replaced by Glassine or other cellulosic wraps. The use of both tin and aluminum are being discontinued in the packaging of cigarets, although the paper substitutes have not proved entirely satisfactory. The foils are needed, in the writers opinion, to protect chocolate bars, cheese, and cigarets from extreme climatic conditions as well as from war gases.

For years cork has served a number of purposes in which it is not easily displaced. Cork is used to make long stoppers for bottles. In composited form it provides an inexpensive elastic cushion and essential lining for bottle caps (crown corks) used in sealing liquids with high gaseous pressure such as ginger ale. A milling grade provides a water- and oiltight gasket for motor engines; and a lower quality or grinding grade is used in making insulation board for refrigeration and other purposes. Cork is harvested largely in Spain, but as a noncontraband material is imported to the United States from Portugal. Long stoppers are disappearing from prescription ware in favor of plastic closures, and cork in bottle closures other than crown corks has been almost entirely replaced by cardboard faced with suitable plastic material notably plasticized vinyl resin calendered on paper-e. g., Vinylite. An example of a bottle cap liner which is being offered for many cold packed products which were formerly sealed with metal foil, rubber hydrochloride, etc., is the plastic wax liner. A plastic wax liner is a white pulpboard heavily coated with a high-melting nonsaponifiable plastic wax. Rubber is not considered for these purposes because of its present shortage.

#### **Conservation of metals**

The shortage of tin arising at the beginning of 1942 caused the manufacturers of cans and glass bottle closures to exert every effort to reduce the amount of tin used in these industries to a minimum and to eliminate it entirely when and wherever possible. For a year previous to any WPB order, a large volume of bottle caps was being converted from dipped tin plate to electrotin plate, thereby saving at least half the amount of tin. The electrolytic tin process in use was developed at the Crown Cork & Seal Company; it is essentially different from a process previously developed in Germany. However, the electrolytic tin closure has now been converted to a tinless closure for the sealing of nonalcoholic and malt beverages, and this is now enforced by WPB ruling. The closures for nonpressure ware are being gradually converted from tinned to tinless steel. The interior of a can is directly exposed to the liquid contents, whereas with a closure such as a crown cork the metal does not need to contact the liquid. Cans that must be sterilized at a high temperature after packing still present a knotty problem that has defied any commercial conversion from tinned or tinless steel. The broader use of electrolytic plate for vegetable cans or can ends is being fostered by WPB's Division of Industry Operations. The electrolytic tin plate carries 0.5 pound of tin per base box (6). Tin is being eliminated to some extent from side seam solders in favor of silver solders made from lead alloyed with a little silver, about 2.5 per cent (9).

A tremendous amount of pressure has been brought to

bear upon the manufacturer of containers to conserve steel. Cans use from thirty to fifty times as much steel and tin for liquids as do glass containers, and from six to thirteen times as much for solids. It has been estimated that in 1941, 3.375,000 tons of steel went into cans, whereas 250,000 tons of steel were used to seal glass containers. Approximately 10 billion glass containers were produced as compared with 25 billion cans (8). The glass container industry is reported as having a 23 million gross capacity available for conservation of critical materials now used in packaging.

Much thought is being given by the conservationists to the comparative amount of steel, tin, and rubber in cans, and that in the glass container closures. A base box of steel plate will yield 265 cans of a quart capacity each. The same amount of steel will, however, yield 14,400 closures for quart-size glass containers. Motor oils and some other commodities can be packed in glass and thus save much steel. Transfer from steel to glass containers is not so advisable where the closures for the glass require as critical a material as rubber. 70,000 tons of steel were used in 1941 for packing tomato juice and cocktail. It has been suggested to pack a portion of this in glass with a crown cork closure and avoid the use of rubber otherwise needed in gaskets for some types of bottle closures. For shipment overseas, glass has the serious drawback of danger of breakage, and the War Department prefers metal. Metal cans have been approved by the War Department as being safe packages against chemical warfare gases. For civilian needs the trend is from metal to glass.

#### Changes in the trend

Significant changes in the trend are apparent daily; e. g., a popular brand of molasses is now packed in glass with a tear-off metal and cork cap instead of a can; spices in cardboard cylinders with metal ends instead of all tin plate canisters; noodle soup mixes in cardboard and cellophane or in very thin metal foil covered cardboard cartons; a popular brand of baked beans formerly in tin is now in glass; some baby foods are now in glass instead of tin.

Frozen egg liquid is now being packed in a cellophane-lined paperboard carton instead of the customary tin can of 30pound capacity. The new container with its leak-proof cellophane bag inside is a rectangular fiberboard box. Its chief advantages are that the frozen eggs may be slipped out in a block and readily melted, it is less costly than the tin can, and it saves much space in car because of its rectangular shape. The current estimate of 1942 output of eggs is 350 million pounds. A little less than 3 billion eggs will be delivered either frozen or dried to bakers, candy makers, restaurants, etc., and to our allies on the Lease-Lend program (4). Each 30-pound can takes 2 pounds of steel, and hence at least a large portion of an estimated 10,000 tons of steel is saved.

In the cosmetic field WPB regulation bans the use of tin plate closures for ointment jars. No new metal can be secured to make more of them (7). There had been a tendency to go from a glass to a plastic container, but scarcity of plastics has reversed the trend. Glass containers with glass closures are receiving serious consideration. The Technical Research Section of the Containers Branch of WPB is reported to be drawing up exact specifications for drug containers, avoiding the use of metal as far as possible. Items considered are those for tooth powder, tooth paste, aspirin, laxative lozenges, etc., in which 35,000 tons of steel are annually used, according to Deputy Chief Charles L. Sheldon (3). The familiar cobalt blue glass container used for many purposes is out, since cobalt was placed on the critical list. It is being replaced by flint glass for the duration of the war. 1

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Paint is now being packed in quart paper cans. The top and bottom are alloy metal disks, but the body is made entirely of cardboard impregnated with an insoluble substance (2). It bears the label "War Emergency Container— Handle with Care". Paint also goes into glass, such a conversion being recently made by the Glidden Company of Cleveland  $(\delta)$ .

Collapsible tubes used 3300 tons of tin in 1939. Although the collapsible tube business has increased enormously since then, the tonnage of tin used this year will be far less than in 1939. Collapsible tubes of aluminum have disappeared from the market. The collapsible tube of tin has been largely replaced by tin-lead alloy tubes or tin-coated lead tubes, thus saving about 70 per cent tin. For certain hygienic preparations pure tin is still considered essential. However, it should be possible to develop a collapsible tube of a leadsilver alloy containing up to 3 per cent silver that would offer the chemical resistance of tin, and to plate this on the inside with a silver-indium alloy. Indium has, however, no official approval as to nontoxicity. Plastic collapsible tubes have been invented but still require perfection.

Containers are being designed to permit economical utilization of transportation facilities. A new method of "clip" packing has been designed by an RCA engineer in the packing of spare radio tubes so that they can be made to fit into spaces

designed by the builders of planes, tanks, and other fighting equipment (10). In production a clip of ten tubes is handled as a unit.

#### **Army specifications**

Tentative U. S. Army Specifications have been drawn up for packaging dehydrated beets, cabbage, carrots, onions, Irish potatoes, sweet potatoes, and yellow turnips. For cabbage and carrots, hermetically sealed 5-gallon square cans in which air has been replaced by nitrogen or carbon dioxide are specified. A choice of containers is provided for the other five dehydrated vegetables. This choice involves fiber drum with kraft asphalt barrier board lining properly sealed, 5-gallon lacquered black metal can with lever lock or friction top, laminated-paper-base sealed bags enclosed in weatherproof solid fiber box, a folding carton with a specially constructed heat-sealing moistureproof inner liner and a highly waterproofed outside wrapper (11).

The specifications for packaging dehydrated vegetables have been recently replaced by a special lead foil package, according to information received from the Office of the Quartermaster General, War Department, Washington. (Tentative Specification for Beets Dehydrated, C. Q. D. No. 72 A, September 4, 1942, supersedes C. Q. D. No. 72, July 18, 1942.) This specification can be applied to white potatoes, sweet potatoes, and rutabagas, inasmuch as the packaging of these items will be identical to that for dehydrated beets, according to official information.

The packaging, labeling, packing, and marking for shipment are covered by Section G of C. Q. D. Specification 72 A. Section G-1 states that the dehydrated product shall be packaged in a laminated sealed bag constructed of films. These films are, briefly:

 $1.\ {\rm Two}$  sheets of Glassine laminated with a permanently plastic laminating agent.



Upper photo shows feeding end; coiler (right) feeds strip into pinch rolls, then into fourstrand slack producer, and up through vertical gas-fired radiant-tube heating furnace (left), in which tin is melted, flowed over steel surface, and then rapidly water-quenched. Lower photo is the delivery end, showing vertical furnace (right), six-strand slack producer (center), and winding reel (left). The speed of this unit is about 250 feet per minute, and the finished product has the typical mirror finish of hot dip plate.

One sheet of a thin moisture-vapor-resistant heat-sealing cellophane laminated to Glassine or to sulfite paper by means of a permanently plastic laminating agent.

3. Two sheets of the thin heat-sealing cellophane laminated together in same manner described under film 2. (Presumably a material such as MSAT cellophane would have these properties.)

The bag may be of flat or gusset style or may be mechanically formed. It is sealed by application of heat or moisturevapor-resistant adhesive. After filling, the bags are closed either by heat sealing or by taping down in the prescribed manner.

Section G-2 describes the outside bag or envelope. This envelope consists essentially of a dense kraft paper laminated with asphalt to a composition lead foil, then laminated on the foil side to a sheet of moistureproof anchored, coated, regenerated cellulose (cellophane) films, by means of a thermoplastic coating on the film, that provides a face to face heat-sealed seam of adequate strength. Section G-3 describes a solid fiber carton of approximately 5-gallon capacity.

The bag is placed in an envelope, the envelope in a carton, and two cartons in a solid wooden box, securely fastened by the strap iron or wire bands. The complete package displaces 1.32 cubic feet. Dehydrated foods will be packed in the manner described above for overseas shipment.

Dehydrated apple nuggets, onions, cabbage, carrots, tomato juice cocktail, and cranberries are still being tentatively packed in cans; the apple nuggets and onions in 5-gallon square cans or round steel cans, or in 30-pound frozen egg or

fruit cans; the dehydrated cabbage and carrots in similar cans, in which air has been replaced by nitrogen or carbon dioxide gas; dehydrated tomato juice cocktail in No. 10 cans, 3 pounds to the can; dehydrated cranberries, powdered, in 1-pound sanitary cans. The specifications on all of these items is flexible so as to permit the consideration or use of protectively coated steel plate instead of tin plate.

The packaging trends during the present emergency will be none too well defined for a year at least, and are at the moment being greatly influenced by Conservation Orders of the WPB. The trends will perhaps be less well defined in packaging for civilians than for Lease-Lend or the armed forces because of the great difficulty that container manufacturers will experience in securing priorities sufficiently high for materials that have been commonly used in the past. The problems of packaging for domestic consumption differ considerably from those in packaging for overseas shipment.

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# Dehydration of meat

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• • • Intensive studies have resulted in methods of dehydration of meat which produce acceptable products. Good quality dehydrated meat reconstitutes readily when water is added. It is suitable for use in any dishes for which ground cooked meat is satisfactory, such as meat loaves, patties, croquettes, soups, and meat pies. One ship will carry dehydrated meat equivalent to three shiploads of boneless beef or ten shiploads of carcass beef.

Best results are obtained by precooking the beef before drying. Various types of dehydration equipment, including warm air, vacuum, drum, and gas dryers have been used. Factors affecting the rate of drying are discussed.

CMALL quantities of dehydrated beef were produced during the first World War and subsequently for several arctic expeditions. Recently, because of the need to conserve shipping space, renewed interest has developed in the dehydration of large amounts of meat for overseas shipment. Early in February, 1942, officials of the United States Department of Agriculture indicated that the Federal Surplus Commodities Corporation would like to purchase considerable quantities of dehydrated meat for Lend-Lease purposes. The meat packing industry was requested to develop methods for the dehydration of meat. On February 10, the Committee on Scientific Research of the American Meat Institute held a meeting to discuss the problem of dehydration of meat. It was agreed that members of the committee would seek to

carry out studies in their respective laboratories, and that the committee would meet subsequently and exchange information.

Intensive studies of methods of meat dehydration were carried out by the research laboratories of a number of meat packing companies, the Research Laboratory of the American Meat Institute, and the United States Department of Agriculture. On the basis of these studies methods have been worked out which will produce satisfactory and acceptable products. The purpose of dehydrated meat is threefold: To conserve shipping space, to conserve tin and other strategic metals if possible, and to furnish a meat product which can be stored safely without refrigeration under varying conditions of temperature and humidity and for prolonged periods.

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#### Dehydrator Used by Swift & Company

The long tube revolves with the meat inside it, resting on louver plates running lengthwise of the interior. Air under controlled temperatures is admitted beneath the louvers and penetrates the meat evenly so that the latter, perfectly dried down to 5 per cent moisture content, sifts out of the far end of the machine into sanitary metal trucks.

By compressing dehydrated meat with pressures of 1500 to 2000 pounds per square inch, the shipping space required may be reduced to less than one tenth of that required for shipment of carcass beef. Boneless beef requires about 36 per cent of the space of carcass beef. Dehydration reduces the space required to about 16 per cent, and compression of the dehydrated beef further reduces the space to about 10 per cent. Thus one ship will carry the dehydrated meat equivalent to ten shiploads of carcass beef.

Good quality dehydrated meat reconstitutes readily when water is added. When cooked it compares favorably in appearance, texture, and flavor with cooked, chopped, fresh meat. The product is suitable for use in various dishes, among which are meat loaves, patties, croquettes, soups, and meat pies. To be satisfactory, dehydrated meat must not deteriorate in storage and should retain as much as possible of the nutritive value of fresh meat.

#### **Precooking of meat**

Best results are obtained by precooking the beef before drying. Thin strips of raw beef have been dehydrated by warm air drying processes without precooking. When the meat is not precooked and is dried in warm air, the finished product does not reconstitute readily when water is added. In raw meat the rate of diffusion of water from the interior of the meat particle to the surface is much slower than in cooked meat. The surface of the particle will dry out and caseharden. A much longer period is required to dehydrate the meat. If the air temperature is kept sufficiently low to prevent casehardening, the drying period is greatly lengthened and suitable conditions for the development of harmful bacteria may prevail.

If the temperature is reduced just below the point at which harmful bacteria will grow, the time required for dehydration will be still further lengthened. The long period required for dehydration under those conditions is sufficient to promote rancidity of the fats and hydrolytic splitting of the proteins. If the temperature is reduced further so that the product is frozen and if it is then dried in vacuum, a product may be obtained which rehydrates satisfactorily and resembles fresh meat closely. The rate of drying is slow and the cost of the equipment relatively high. When raw meat is dehydrated in the frozen condition, the fat- and protein-splitting enzymes are not destroyed. Data are not available to show that meat dehydrated in the frozen state will keep satisfactorily for long periods when stored without refrigeration.

Precooking may be carried out in an open steam-jacketed kettle equipped with a stirrer. The meat is cut into approximately 2-inch cubes and precooked with little or no added water. During cooking in an open kettle the moisture content of beef may be reduced from 70-72 per cent to around 50-55 per cent. After cooking, the product is ground in a food chopper equipped with a  $1/e^{-1}/s$  inch plate. All of the juices are retained in the ground product. Precooking may be carried out in a pressure cooker. Then the juices are added back to the ground product before it is dried. Federal specifications require the beef to be precooked a minimum of 30 minutes at not less than 165° F. internal temperature.

A third method of precooking consists in putting the meat through a meat chopper with a  $1^{1}/_{s}$ -inch plate and then passing it over a steam-heated drum dryer similar to those formerly used extensively for drying milk. The drums are set about 0.1 inch apart, and the product is cooked for about 50 seconds. The partially dried chips are then dried in an air dryer. This results in larger sized particles.

In addition to increasing the rate of diffusion of moisture from the interior of the meat particles during drying, the precooking, if carried out in an open kettle or drum dryer reduces the moisture content of the meat. The precooking also inactivates enzymes and destroys nonspore-forming pathogens if any are present.

After precooking, the product is dried promptly to a moisture content of not to exceed 10 per cent in any particle. The precooked product should not be held for longer than 2 hours at a temperature within the range of  $60^{\circ}$  to  $160^{\circ}$  F. in order to prevent the development of food spoilage organisms.

#### Dehydration equipment

Many different types of dehydration equipment have been proposed and tried. They include various types of warm air dryers, vacuum dryers, drum dryers, and gas dryers. For large-scale and efficient operation the continuous system of drying is desirable. It has many advantages over the batch system. The continuous system is more economical because it requires much less labor. Also, since there is less human handling of the product, there is less opportunity for contamination with food spoilage organisms.

AIR DRYERS. Satisfactory products have been made with the tunnel and rotary types of warm air dryers. One of each of these types will be described in more detail later.

ROTARY DRUM DRYERS. Drum dryers of the type formerly used extensively for drying milk have been tried experimentally to dehydrate meat. The fresh meat was first cooked in a steam-jacketed open kettle and then ground through a meat



Space Is Saved by Swift & Company's Methods of Processing Pork

Fresh pork sides were sent to Europe during the first World War. Ten ships loaded with sides, kept under refrigeration, were replaced early in the present war with 7.5 ships carrying the same amount of meat in special packages of bone-in cuts, also refrigerated. Dehydration of the pork has cut the space requirements for the same amount of meat to 1.85 ships. The compression packing methods cut the requirement to 1.3 ships. Dehydrated meat keeps fresh on long ocean voyages, when properly packaged, without refrigeration.

chopper equipped with a 3/16-inch plate. The ground product was then passed over the steam-heated drum dryer. The dehydrated products consist of thin flakes. The product is more difficult to compress into compact blocks than when dried in air dryers. Although the drum-dried product is fairly satisfactory, it is not so good as those dried in air.

**VACUUM SHELF** DRYERS. Experiments with vacuum shelf dryers have demonstrated that a good quality of dehydrated beef can be produced by this method. Fresh beef chucks were ground through a meat chopper equipped with a 3/1-inch plate. The ground meat was cooked (without the addition of water) in a steam-jacketed kettle equipped with a mechanical

stirrer. The product was brought to 165° F. and cooked at that temperature for 30 minutes. During the cooking the product, which originally contained about 68 per cent moisture, lost 25 per cent of its moisture. After cooking, the meat was dried in a vacuum shelf dryer in a 4-hour cycle from loading to unloading. The temperature of the dryer shelf ranged from 165° to 185° F. A 29.5inch vacuum was used. The temperature of the meat ranged from 55° to 160° F. during the drying. The final product contained about 30 per cent fat and 8.5 per cent moisture.

VACUUM MELTERS. Vacuum steamjacketed melters of the type used for rendering lard have been used experimentally to dehydrate beef. The beef is cut in small pieces, placed in the melter, and precooked under pressure. Then the vacuum is applied and the product is dehydrated. The final product is in a finer state of subdivision, and the flavor is not so good as that which is properly air-dried.

AIR-CONDITIONED SMOKEHOUSES. Dehydrated beef and pork comparable in quality to the products produced in warm air dryers have been produced experimentally in air-conditioned smokehouses. The fresh meat was precooked in a steam-jacketed open kettle and subsequently ground in a meat chopper equipped with a 3/16-inch plate. The product was then dried on trays in the smokehouse without the use of smoke. This process has the serious disadvantage of the batch process. The labor costs would doubtless be much higher than in a continuous process.

## Factors affecting the drying rate in air

Dehydration of meat in a moving current of warm air. from the viewpoint of the material, represents evaporation of moisture from a complicated system. Initially the rate of removal of water should be similar to that of an equivalent surface of water containing the same solutes. The rate is determined by the difference in water potential between the surface of the meat particles and the air and by the rate of diffusion of the moisture into the surface layer. As long as there is rapid diffusion and the surfaces of the particles remain wet, the temperature of the meat particle will not rise above that of the wet bulb temperature of the air and may be far below that of the dry bulb temperature. For this reason the air temperature, during the early stages of drying, may safely be much higher than the temperature which would injure the meat, provided there is adequate circulation of air. Since diffusion of moisture from the interior of the particle becomes a limiting factor in the later stages, the safe air temperatures in the final stages are much lower than in the initial stages of drying. By precooking the meat, the colloidal properties of the meat proteins are altered and diffusion of moisture to the surface of the particle is greatly accelerated.

Drying temperatures should be as high as possible to increase the thermal efficiency of the process and to reduce the opportunity for bacterial development, but not so high as to injure the quality of the product. In general, lower drying temperatures will yield a product of better quality if the drying time is not prolonged. Temperatures above  $150^{\circ}$  F. may result in some deterioration in quality although products of good quality have been produced with final drying temperatures from  $160^{\circ}$  to  $165^{\circ}$  F.

Reducing the size of the particle increases the rate of drying, due to the increased surface and the shorter distance of



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diffusion of moisture from the center of the particle to the surface.

Another important factor affecting the rate of drying is the velocity of the air. High velocities increase the rate of drying. If the air is driven through a bed of the granular material, the depth of the layer of meat will affect the velocity of the air. After the meat is partially dried, the bed is more porous and an equal load will offer less resistance to the current of air. The effect of air velocity on the rate of water loss is more marked during the initial stages of drying, since diffusion of moisture from the interior of the particle becomes a limiting factor in the later stages.

The amount of fat present influences the rate of drying. In the initial stages the effect is not marked, but in the final stages high fat content retards the rate of water loss markedly. The higher the fat content, the earlier in the period of drying it begins to retard the rate of drying. This may be due to the fact that, after the early stages of drying, the temperature rises high enough to melt the fat. The melted fat then covers an increased surface and retards evaporation.

#### F. S. C. C. specifications for dehydrated beef

The Agricultural Marketing Administration of the United States Department of Agriculture announced on July 1, 1942, that offers would be received for sale of dehydrated beef. The specifications given in Form FSC 1719, Dehydrated Beef—Offer of Sale, Program GCP, are as follows:

SPECIFICATIONS: Dehydrated beef shall consist of beef derived from the entire carcasses of boned cattle of U. S. canner grade or better. Meat from bulls shall be excluded. Closely trimmed beef cheek meat and beef head meat may be included up to 3 per cent of the total meat used. The meat shall be reasonably free from blood clots, bruises, stringy fibrous tissue, tendons, and sections of large blood vessels.

Fat content of the finished product shall not exceed 30 per cent.

cent. Salt may be added to the meat to the extent that the finished product shall average not more than  $3^1/_2$  per cent sodium chloride.

The meat shall be precooked a minimum of 30 minutes at not less than 165° Fahrenheit internal temperature.

After precooking, promptly dry the meat until the moisture content of the dehydrated meat product does not exceed 10 per cent in any particle when placed into the container.

The dehydrated beef shall be packed as tightly as possible into rectangular or round tin cans, hermetically sealed with or without vacuum, and shall be packed into containers meeting the requirements of Federal Specifications for canned meat for export.

On July 30 the Federal Government awarded the first contract for 80,000 pounds of dehydrated beef.

#### **Commercial processes**

Two types of continuous drying equipment have received prime consideration for commercial operations. One is a rotary type dryer and the other a tunnel type with an endless belt conveyor. Both types use steam radiators for heating the air. At least 80 pounds steam pressure is required for the rotary dryer. Higher steam pressures are desirable for both types of dryers although the tunnel dryer may be operated with 10 pounds exhaust steam.

ROTATING DRUM DRYER. The fresh beef is passed through a rotary meat chopper which divides it into approximately 2-inch cubes. The meat is then dropped into an open steamjacketed kettle, equipped with a mechanical agitator and having a capacity of 1500 pounds of chopped meat. Four kettles are needed to supply one rotary dryer (7 feet 11 inches in diameter and 24 feet long) having a capacity of 1000 pounds of finished product per hour. Just sufficient water is added to prevent sticking of the meat to the kettle, and the beef is then cooked with constant agitation at a temperature not lower



Reduction in Volume Achieved by Dehydrating Pork: the Twenty-eight Cans Hold All the Meat of the Two Pork Sides, Which Dress Out to 169 Pounds

than  $165 \,^{\circ}$  F. or higher than  $175 \,^{\circ}$  F. for not less than 30 minutes. The precooking reduces the water content of the beef from about 72 to about 50 per cent. It is necessary to reduce the moisture content of the meat to 50–55 per cent of moisture in order to dry it in the rotary dryer.

The cooked product is then dropped into a steam-jacketed hopper and conveyed mechanically to a meat hasher where it is ground with  $^{1}/_{s}$ -inch plates and at a temperature of approximately 155° F. The precooked beef is fed directly from the hasher into the rotating drum dryer.

Air heated to about  $300^{\circ}$  F. is passed through the horizontal drum dryer at a velocity of about 800 feet per minute. The drum dryer is equipped with louver-like vents. The rotation of the drum tumbles the meat as it passes through the dryer and permits the air to pass through the tumbling mass of meat. The meat reaches the outlet end of the drum in about 2 hours with a moisture content of 10 per cent or less. The air discharge temperature is about  $150^{\circ}$  F. The product is then pressed in airtight containers and sealed under vacuum.

TUNNEL BELT CONVEYOR DRYER. This dryer is built in units 6 feet long. Ten units have an estimated capacity of 1000 to 1300 pounds of dehydrated beef per hour. The length of space required for the installation may be reduced by placing five units directly above the other five units. Each drying unit is equipped with a centrifugal fan. The equipment is designed to permit the desired amount of recirculation of air. Air velocities through the meat of 200 feet per minute are obtained.

Each of the two five-unit sections is equipped with a perforated metal plate sectional conveyor which is 10 feet wide. The purpose of the two-stage drying is to maintain an increased drying capacity through a more advantageous depth of loading. The wet material containing about 55 per cent of moisture is loaded to a depth of approximately 1.5 inches, equivalent to 2 pounds of meat per square foot, in the first stage. It leaves the first stage and enters the second stage at about 34 per cent moisture, where the depth of loading is increased to 4.5-5 inches, equivalent to 9.5 pounds of meat (34 per cent moisture content) per square foot. A greater depth of loading is possible in the second stage because the air penetrates the meat more readily after the meat is partially dried. Circulation and penetration of the air through the meat is aided by a constant static pressure of 0.6 inch in both stages.

The precooking and handling of the meat prior to drying is similar to that described for the rotary dryer. If desirable, products containing more moisture can be dried in this type of dryer than in the rotary dryer. The precooked chopped meat is fed onto the belt conveyor by means of an automatic oscillating conveyor which deposits the meat at a uniform depth.

Tests made on meat dried experimentally on both types of equipment indicate that dehydrated meat of equal quality can be made with either type of equipment.

#### **Dehydration of pork**

Federal officials have indicated that only limited quantities of beef will be available for dehydration. Plans are being made to produce large quantities of dehydrated pork. A program has been designed to increase capacity to 60,000,000 pounds annually in the near future.

Federal specifications for dehydrated pork have not been issued. In general, the processes described for dehydrated beef appear to be suitable for pork. However, due to the higher fat content and the differences in physical qualities of pork tissues, some modifications may be necessary. It may be necessary to remove some of the fat in the process of precooking. The precooking period may require a longer time. Experiments indicate that, after precooking, the product may be pressed to remove fat and moisture. After the fat is skimmed off, the water extract may be concentrated in a vacuum evaporator to a sirupy consistency. The pressed residue may be ground through a hasher and dried. The evaporated sirup is then added to the dried residue. In this manner a finished product may be produced containing about 50 per cent protein, 40 per cent fat, and about 10 per cent moisture.

KEEPING QUALITY. Sufficient data are not available to indicate how long dehydrated pork will keep. Experiments indicate that dehydrated beef will not become rancid for long periods if the product is packed tightly in hermetically sealed packages. It may be necessary to pack dehydrated pork under vacuum or to use antioxidants in order to prevent rancidity.

Extensive studies carried out by the Department of Bacteriology of the University of Chicago, in cooperation with the Agricultural Research Administration of the United States Department of Agriculture, have shown that from a bacteriological standpoint dehydrated meat made in accordance with the Federal Specifications is safe and will remain so when stored without refrigeration in hermetically sealed containers.

PACKAGING. Until suitable nonmetallic packages are developed and proved satisfactory, it will be necessary to use metal cans. Intensive studies are underway to test the keeping quality of dehydrated beef and pork when packed in various metallic and nonmetallic containers and subjected to wide variations in temperature and humidity.

## Stabilization of fats and fatty foods

H. S. MITCHELL AND H. C. BLACK, Swift & Company, Chicago, Ill.

• • For the stabilization of fats and fatty foods, materials naturally occurring with food products have received most attention since such substances are unlikely to have toxic effects. However, one antioxidant, not occurring with food materials, has been shown to be an effective stabilizer for meat food fats. It is gum guaiac obtained from a tropical tree. It is entirely innocuous physiologically and is a practical commercial antioxidant for lard. It also shows promise for the stabilization of packaging materials for fats and fatty foods and for the stabilization of dehydrated meat products.

**F**ATS and fatty foods are attacked by oxygen, resulting in an oxidative deterioration known as rancidity. Only meager information exists on the reactions that take place. It is well established that they are autocatalytic in nature. They are accelerated by heat, light (especially ultraviolet), and metals such as iron and copper and their salts. The rate is lowered by antioxidants. The refining procedures necessary to produce shortening acceptable to present-day consumers remove large percentages of the natural antioxidants, with the result that refined oils and fats exhibit less resistance to rancidity than do the crude materials.

Oxygen is absorbed by the unsaturated bonds of the fatty acids, with formation of peroxides, and finally certain alde-

hydes and ketones are produced by rupture of the carbon chain at the oxidized bonds. The degree to which the reaction has progressed determines the extent of the spoilage. There is a latent or induction period of variable length during which small amounts of oxygen are absorbed and only slight organoleptic changes are noted. This is followed by a rapidly accelerated oxygen absorption accompanied by the appearance of the so-called rancid odors and flavors. The final stage is a breakdown of the oxidized bonds, which is accompanied by strong acrid odors.

The logical means of preventing these reactions is either protection from oxygen, as exemplified by vacuum packing, or by the use of antioxidants. The former involves considerL

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able difficulty and expense, and does not find application in a wide variety of food products. The use of antioxidants in fats was attempted long ago. Gum benzoin was employed nearly a century ago to prevent rancidity in lard ointments, and the Indians apparently used the bark of certain trees to preserve bear grease (10).

## Antioxidants naturally occurring with food

No real progress was made in the field of antioxidants until about twenty years ago, when Moureu and Dufraisse (11) found that hydroquinone had an inhibitory effect on the oxidation of acrolein and benzaldehyde. Since then a large number of compounds have been shown to possess varying degrees of antioxidant properties for oxidizable materials such as mineral oils, gasoline, rubber, and glyceride oils. Materials naturally occurring with food products have received most attention for stabilization of fatty foods since such substances are unlikely to have toxic effects. The first of these was lecithin, the name applied to the phospholipides of soybean oil, which was proposed by Bollman in 1923 (1). It finds some application not only as a stablilizer but also for improving emulsification and frying properties. Carefully purified lecithin possesses no antioxidant activity, and Olcott and Mattill (20) showed that the cephalin fraction of the phospholipides carries the inhibitory action.

Portions of the cephalin molecule have been patented separately. The phosphoric acid fragment is covered by Eckey (5). Royce (21) patented cephalin minus the fatty acid in the alpha position, and Epstein and Harris (6) claimed the molecule minus the cholamine and one of the fatty acid radicals. Thurman (22) obtained patents on the use of cottonseed and corn oil phospholipides as antioxidants and emulsifiers on the basis that these materials are less likely to oxidize in that they are more saturated than soybean phospholipides.

Certain plant pigments have been shown to be antioxidants. Newton (14) indicated that carotenoid pigments, or some material closely associated with them in nature, have antioxidant properties under certain conditions, and that the stability carried through into the baked goods made from the fats. The work of Olcott and Mattill (19) showed carotene to be a pro-oxidant. The difference in results lies in the fact that carotene retards oxidation after the induction period has run its course, and the latter authors were concerned with the induction period only, while Newton considered the whole course of the reaction.

Other materials associated with vegetable oils which have received attention as antioxidants are the "inhibitols" of Olcott and Mattill (18). These are materials, nonsterol in nature, which are concentrated in the unsaponifiable fraction and which depend for their activity on free hydroxyl groups. Later it was shown that pure tocopherols possessed marked antioxygenic activity (17). Recently Olcott concluded that some, if not most, of the antioxidant properties of unsaponifiable fractions of vegetable oils is due to tocopherols (16). Tocopherols are effective in lard and purified esters of fatty acids but not in vegetable oils. Golumbic (7) recently showed that chroman and coumarin derivatives having a hydroxyl group but no aliphatic side chains are effective antioxidants.

The fractions molecularly distilled from vegetable oils and patented by the Eastman Kodak Company (4) contain large percentages of tocopherols.

Grettie ( $\theta$ ) showed that hydrogenated sesame oil has antioxidant properties in lard and vegetable oils. Wheat germ oil, which probably owes its effect to the synergistic action of tocopherols and phospholipides, has been proposed.

Turning from the materials associated with oils, we note that the Musher Foundation (12) has supported a considerable amount of study on the practical application of oat flour as

an antioxidant. It has been suggested for the stabilization of butter, ice cream, potato chips, and many other fat-containing foods, as well as for packaging materials for them. The nature of the oat flour antioxidant is not definitely known, although it is claimed to be a protein-fat complex (3). More recently the Musher Foundation (13) obtained patents on the use of many substances and combinations of substances as antioxidants. Among these are preparations from cereals, sugars, grains, milk solids, oils, yeast, animal tissues, legumes, and grasses.

The dicarboxylic acids occurring in fruits were investigated by Greenbank and Holm (8). They found maleic, tartaric, and citric acids to be effective in lard and vegetable oils. It has since been established that, to be effective, those acids containing more than three carbons must also contain a hydroxyl group.

Combinations of antioxidants have been shown to give protection in excess of that expected from the results with either one alone (16). Combinations of inhibitols with acids and of phenols with acids are especially effective.

One antioxidant, not occurring with food materials, has received considerable attention. It is gum guaiac, proposed by Newton and Grettie (15). It is obtained from a tropical tree, *Guaiacum officinalis*, which grows in Central America and the West Indies. Extensive tests carried out by Carlson at the University of Chicago have proved it to be entirely innocuous physiologically (2). It is effective in meat food fats but shows only slight antioxidant activity in vegetable oils. Its stabilizing effect carries through into the baked goods prepared from the fats.

Table I gives comparative results obtained in this laboratory with several antioxidants on lard and cottonseed oil. Pyrogallol is the most effective in lard, while citric acid has the greatest effect on cottonseed oil. The combination of gum guaiac and phosphoric acid produces remarkable stability. This substantiates earlier results on the synergistic effect of phenols and acids.

Table I.	Comparative	Antioxidant	Properties
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	Hr. by Active Oxygen Method	
	Lard	Cotton- seed oil
Control Control + 0.01% pyrogallol Control + 0.002% phosphoric acid Control + 0.002% citric acid Control + 1.0% wheat germ oil Control + 0.05% a-tocopherol Control + 0.05% gum guaiac Control + 0.05% gum guaiac Control + 0.05% gum guaiac + 0.002% phos- phoric acid Control + 0.05% gum guaiac + 0.002% citric	5 100 6 8 20 33 8 20 36	12 14 18 20 14 15 14 15 19
acid	22	20

#### Gum guaiac

During two years of commercial use, gum guaiac has proved to be a practical and effective stabilizer for lard. It has been used in the stabilization of a highly processed (bland) lard, which without the protection of guaiac would have a stability of 3 to 5 hours by the active oxygen method. The lard treated with 0.05 per cent guaiac ranges from 15 to 25 hours in stability. Samples remain in good organoleptic condition for over a year at room temperature. Crackers prepared from the stabilized lard keep 16 to 20 days at 140° F. as compared to 2 to 4 days for crackers made from unstabilized processed lard.

The increase in lard stability brought about through the use of gum guaiac may be of great commercial importance to the producer as well as to the consumer. Since ordinary packaged lard must be held under refrigeration, it can be displayed and sold only on the meat counters. The stabilized lard is handled on the grocery shelves along with other shortenings. Stabilization with an antioxidant rather than by hydrogenation retains all of the excellent nutritional properties, such as the high digestibility and essential fatty acid content of lard.

Gum guaiac is easily incorporated into fats even though it is not readily soluble in them. It can be added to the steam or dry-rendering tanks during the rendering period. It can also be incorporated into the fats after rendering by the use of a mutual solvent-that is, one which will dissolve the gum and, in turn, dissolve in the fat. The gum is dissolved in the solvent and filtered to remove the solid material consisting of small particles of sand, bark, and wood which the crude material usually contains. The solution is then added to the fat, preferably as it is maintained under a vacuum and at a temperature sufficiently high to vaporize the solvent.

Gum guaiac has utility for the stabilization of animal fats during storage. The keeping qualities of good lard, for example, may drop 50 to 100 per cent during a storage period of 6 months to 2 years. Guaiac-treated lard going into storage with a stability of 20 to 25 hours will have a much better stability at the end of the storage period than untreated lard entering storage with a stability of 8 to 12 hours.

Interesting results have been obtained on the stabilization of other meat food fats with guaiac. Results obtained with oleo oil and on crackers made from it are as follows:

	Hr. by Active Oxygen Method	Days before Crackers Are Rancid at 140° F.
Original Oleo oil	9	27
Original + 0.1% gum guaiac	52	52

This antioxidant also has good stabilizing properties in chicken fat. Results obtained on addition of the guaiac after rendering, as well as during the rendering period are as follows:

	Hr. by Active Oxygen Method
Rendered chicken fat	22
Same + 0.1% gum guaiac	35
Chicken fat rendered with 0.1% gum guaiac	100

The present nonavailability of tinware for food packaging has resulted in the introduction of a number of dehydrated foods. It is the consensus in many quarters that certain dehydrated products may continue in demand after the war. Dried soups have already reached a sizable volume. Scarcity of shipping space has made necessary the dehydration of meats for shipment abroad and for concentrated army rations. Orders have already been placed for quantities of dehydrated beef, and it is said that dried pork will be produced in much larger volume.

Gum guaiac has a probable further application in these dehydrated foods. The fats in such foods tend to turn rancid and thus harm the qualities of the products. The stabilizing effect of guaiac on chicken fat has already been indicated. Tests now underway show that some increased keeping quality is imparted to dehydrated beef by guaiac, and that the storage life of dehydrated pork is increased markedly. Gum guaiac is heat stable and, therefore, withstands the cooking and drying processes used in the preparation of the dehydrated materials.

Another application of gum guaiac is the stabilization of paper packaging materials for fats and fatty foods. This takes on an added importance during the present shortage of metals for food packages. It can be incorporated into certain papers during their manufacture. One application is in liners for lard and shortening cartons. Here the thin layer of fat which is absorbed by the liner and carton quickly becomes rancid (in 3 months at 75° F.). The presence of the antioxidant in the paper liner and carton retards this appreciably (to 6 months at 75° F.). Experiments are underway on various other packaging materials for meats, poultry, and dairy products.

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Picking Prunes for Dehydration

(See article on page 53)

# Dehydration of fruits and vegetables

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• • The dehydration of vegetables for the Army, Navy, and Lend-Lease has recently assumed important proportions. Forced-draft tunnel dehydrators using trays and controlled temperature are generally usually employed. General quality of the dried products is better than of those supplied the A. E. F. in 1917–18 because blanching to inactivate enzyme activity and drying to a low moisture content give dried products of better initial as well as keeping quality. The central air discharge, combination parallel and countercurrent forced-draft dehydrator in use in Canada is efficient for vegetable drying.

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Vitamin C is largely lost in dehydration and subsequent storage of vegetables; in some cases carotene is unstable to oxidation, and much may be lost. The B vitamins are quite stable during drying and storage. Vegetables should be dried to low moisture content to prevent rapid deterioration in storage.

In the dehydration of fruits undesirable color changes and loss in C and carotene can be minimized by steam blanching, although darkening and loss of these vitamins are more rapid in storage than is the case with the sulfured fruits. Exposure to burning sulfur fumes is the customary pretreatment. Dehydrated fruits require less sulfur dioxide for satisfactory color retention than do the sundried. Much of the California prune crop is now dehydrated instead of being dried in the sun. Most California apricots, peaches, pears, and rasins are still dried in the sun, although in normal years considerable quantities of sulfur-bleached seedless grapes and pitted, peeled clingstone peaches are dehydrated. Apples are dehydrated or "evaporated", various types of dryers being used.

Inhibition of enzyme action is highly important in the dehydration of vegetables and fruits.

THE dehydration of foods, particularly of fresh vegetables for use by the Army, Navy, and Lend-Lease, has come into prominence during the past year. As long ago as June, 1940, at the Chicago Convention of the Institute of Food Technologists, Louis Johnston, Assistant Secretary of War at that time, stated that undoubtedly the Army would need dehydrated foods for use in prospective overseas operations. That was eighteen months before Pearl Harbor. He advised food technologists to give more attention to food dehydration in order that the food industry would be prepared when the Army should need dehydrated foods in quantity and on short notice. His words were prophetic, for even before December 7, 1941, the Quartermaster Corps had become active in fostering research on and development of vegetable dehydration. Colonel Paul P. Logan of the Quartermaster General's Office has been particularly active in promoting vegetable dehydration, and the QMC Research laboratory in Chicago has also given much attention to dehydrated foods.

With the approval of Colonel Logan's office, Mrak and Cruess prepared a bulletin in 1941 (17) on the dehydration of vegetables which was issued by the Quartermaster Corps. Research on vegetable dehydration has been underway in this laboratory for the past two and a half years, more or less a resumption of similar investigations begun in 1917 and extending to about 1925.

Dehydrated foods, including vegetables, are not new. According to Prescott (20) dried vegetables compressed into briquet form were used, somewhat sparingly, by the Union forces to prevent scurvy during the Civil War, although the methods of drying then in use probably retained practically none of the ascorbic acid.

During World War I, according to Nichols and associates (19), about 8,900,000 pounds of dehydrated vegetables, chiefly potatoes, soup mix, carrots, and onions were shipped to the A. E. F. in France. A. E. F. veterans state that the dehydrated vegetables served in France were usually tasteless, tough, and often haylike in odor and flavor, and that they never wish to see dehydrated vegetables again! Probably the practice of drying vegetables, except potatoes, without blanching before drying caused the toughness, undesirable flavor and odor, and poor keeping quality.

After the close of the war, several well-fin inced companies, such as Wittenberg-King, E. C. Horst Company, Caladero Products, California Evaporated Products Company, and others, attempted to market dehydrated vegetables to the civilian public. All failed financially or gave it up as an unprofitable venture. Again failure to blanch before dehydration was largely to blame. Also, improper packaging and allowing insect infestation and absorption of moisture, with consequent darkening and oxidative changes, were contributory causes. The price per pound was necessarily high and must always be so because of the high drying ratio. Thus a pound of dried vegetables has to retail at perhaps 40 cents to a dollar a pound, depending on the variety, in comparison with 2 to 10 cents a pound retail for the fresh vegetables in season. Probably proper educational advertising can overcome this last obstacle.

During the past ten years or more, several dehydrators have produced dehydrated garlic and onions profitably as flakes and as powder. These are used commercially in flavoring



Spinach before and after Drying

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meat products, canned soups, and other food products. Paradoxically, they are the exception to two rules. They are not blanched, as their flavoring power is greater unblanched, and they have been quite successful commercially.

Still more recently, dehydrated vegetable soup mixes have reappeared on the civilian retail market. These have proved fairly popular, largely, no doubt, because they have followed the dry chicken noodle soup mix, packed in the aluminum foil container. With the use of aluminum foil and Pliofilm prohibited for civilian needs, it will be interesting to see how the soup mixes "stand up" on the grocer's shelf in the sub-



In This Equipment Prunes Are Dipped in Dilute Sodium Hydroxide Solution to Hasten Hydration

stitute package. At least some of the vegetable soup mixture is not blanched; the writer has found among samples bought for home use several that had darkened and become haylike in odor. Blanching is essential in this case and in most others. In a letter addressed to a recent dehydration conference at the University of California, Colonel Logan stated that the Army and Navy would need about 25,000,000 pounds of dehydrated vegetables in 1942. This means 12,500 tons on the dry basis or about 150,000 tons on the fresh basis—quite an important quantity, although not great in comparison with the 200,000 tons of raisins or prunes produced annually in California. Lend-Lease is also taking a considerable quantity. The Army's needs for 1943 will be much greater than for 1942. Great activity still exists in expanding present and establishing new dehydration facilities.

Vegetable canneries have the steam power needed for blanching, peeling, and furnishing heat for drying and the necessary preparation equipment, experience, and trained personnel. In the Middle West and East (where fruit dehydrators do not exist for conversion to vegetable dehydration) vegetable canners seem to be the logical ones to undertake expansion of vegetable dehydration in that area. If cans become scarcer, canners may be forced to dehydrate much of the peas, corn, tomatoes, spinach, and other vegetables now canned. Consequently the leading canners are intensively studying vegetable dehydration. Very few (so far as this author is aware) have yet undertaken vegetable dehydration commercially.

In California prune and grape dehydrators have been converted to the dehydration of vegetables. It has been necessary to install blanching and peeling equipment, belt sorters, slicers, etc., as these are lacking in the usual fruit dehydrating plant.

#### **Vegetable variety and freshness**

As is the case for frozen pack and for canning, not all varieties of a given vegetable are equally suitable for dehydration. Some carrots are pale in color and low in carotene; others are woody or have a light colored core. In our tests and in commercial practice the Imperator and the Red Core Chantenay have proved satisfactory. Among onions the mild flavored varieties, such as the Bermuda, are much less desirable than the more pungent varieties, such as the Ebenezer. While the Savoy, a green leafed variety of cabbage, is preferable to the Copenhagen Market and other solid headed varieties, it is more difficult to grow, gives lower yields, and hence is scarce in the market. The Netted Gem potato has proved best of the varieties commonly grown in the West because it is not "soggy" or "sticky"; it gives a white (not yellow) dried product and the dried product cooks well.

Similar considerations hold for other vegetables. The United States Department of Agriculture has a comprehensive program underway on varietal tests, and similar tests are being conducted by the University of California and research institutions of other states.

After they are picked, leafy vegetables rapidly lose vitamin C; spinach may lose all of it in less than 3 days, according to Chace (4). Flavor, particularly of peas and corn, rapidly deteriorates after picking; they should be blanched and placed in the dehydrator within 3 hours or less after being picked.

Potatoes, onions, carrots, turnips, and pie pumpkin or pie squash can be stored under favorable conditions for some time, but even potatoes and onions are best if used within a week after harvest. Long storage results in serious deterioration in quality and dietary value. Fresh cabbage has only a short storage life and should be dried within less than a week after harvest. Obviously such vegetables as tomatoes, celery, chard, peppers, and string beans must be dried while fresh, as they soon wilt.

Chace (4) states that "with careful handling one can put in the hands of the Army or the general public a product (dehydrated) higher in vitamins than the housewife can ordinarily obtain from the local grocer (fresh)". Therefore the dehydrator should be located near the source of raw material.

#### Mechanical preparation for drying

PEELING. At present root vegetables and tubers are usually peeled mechanically in the familiar abrasion type power-driven potato peeler. Loss of edible tissue is heavy, as the abrasion surface of the peeler cuts deep into the flesh in order to remove wrinkles, eyes, etc., and thus reduce the amount of trimming required.

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For many years canners have lye-peeled peaches, carrots, and sweet potatoes in boiling sodium hydroxide solution. Our tests made two years ago showed that white potatoes can be peeled in similar manner in hot 10-15 per cent sodium hydroxide solution. Peaches require only a 1-2 per cent solution and carrots about 3 per cent. Regular commercial sweet potato or peach lye-peeling equipment can be used. One dehydrator devised a simple lye peeler consisting of a rectangular iron tank heated by steam, through which the white potatoes or carrots are conveyed continuously by a metal draper. A rotary washer with powerful jet sprays of water removes the disintegrated peel and lye solution.

We find that a rinse in dilute  $(0.5 \pm \text{ per cent})$  hydrochloric acid solution followed by a water rinse is beneficial for lyepeeled white potatoes in promoting white color.

Pimentos are roasted in a natural gas flame or in a rotating heated steel drum to char the skins, which are then removed in sprays of water. Potatoes and root vegetables are flamepeeled in Canada for dehydration. Recently Chace and associates (4) applied Canadian technique experimentally.

Lye peeling causes much less loss and makes less hand trimming necessary than does peeling of potatoes and carrots by the usual abrasion method.

Onions present a difficult problem. The outer paperlike husks must be removed. One large operator trims off the butt and blossom ends by hand with peach-pitting spoons. The onions are then sliced in a slicer of special design that does not clog with the "paper husks". After drying, the husks are removed mechanically by air suction. Lye peeling is not practicable in this case. A hot water dip followed by a short spin in an abrasion peeler has been suggested as a method of removing the husks. Some operators remove them by hand, a costly procedure.

SUBDIVIDING. For cabbage the usual kraut slicer works very well. The Army prefers potatoes in shoestring strips about  $\frac{3}{19} \times \frac{1}{4}$  inch in cross section. Satisfactory machines have been devised for this operation by the canning machinery companies. Some root vegetables are similarly prepared. Potatoes in slices are apt to mat together and thus dry



Courtesy, Anabolic Food Products, Inc. Traying Vegetables for Dehydration

slowly; sliced carrots, however, curl during drying and hence are not so likely to mat. Potatoes, carrots, and beets are diced in pieces about  $\frac{1}{2}$  inch in diameter. Canners' machinery already in use has proved very satisfactory for dicing.

Tomatoes are peeled and sliced or cut in segments before drying, or cut and dried without peeling. Small paste varieties (Italian plum and pear-shaped varieties) may be dried whole after peeling, or cut in half lengthwise and dried without peeling.

#### Chemical treatment before drying

SULFURING. The British military prefers that shredded cabbage be wet with dilute bisulfite solution before drying in order to retain vitamin C, otherwise lost in large measure by oxidation. Tomatoes lose much vitamin C unless exposed to sulfur dioxide fumes or dipped in a bisulfite solution before drying. Their color is much brighter and more intense if sulfured or sulfited.

The extent of  $B_1$  loss from the sulfuring or bisulfite dip has not been determined. However, both cabbage and tomatoes are more useful in the diet for their C than for their  $B_1$  content.

There seems no need for sulfuring other vegetables, except possibly onions and garlic to prevent darkening during storage.

BLANCHING. Enzymes are of great importance in the drying of vegetables and in subsequent storage (9, 10). Blanching (scalding) has for its purpose the inactivation of these agencies before drying. It has been difficult to persuade dehydrators that enzymes are of any consequence and that blanching is essential. In fact, one operator said: "Blanching? Oh, we got away from that years ago!" But the lines in the old A. E. F. song, "they feed us carrots every day, that taste just like alfalfa hay", were probably written by some doughboy in 1917 who had been fed unblanched dehydrated carrots. Incidentally, the ditty is correct in this case.

As early as 1919 this laboratory was on record (6) as recommending the blanching of most vegetables. In many re-

spects the situation is parallel to that of the freezing storage of vegetables. Those who first engaged in freezing vegetables did not blanch or scald them. Later in storage the vegetables acquired a stale or haylike odor and flavor and in time became inedible.

Based on previous experience with blanching of vegetables and subsequent investigations on freezing storage, Joslyn and Cruess (14) recommended the blanching of vegetables for freezing storage in 1929, a recommendation that was quickly put into effect. Diehl and Berry (12) also pioneered in this field.

Investigations of the past two years amply confirm recommendations of 1919 and 1929. Blanching is essential to proper retention of color, flavor, aroma, and texture in dehydrated vegetables. The unblanched are tough, cook excessively slowly, and rapidly deteriorate in color, flavor, and odor during storage. Vitamin C and carotene retention are greatly enhanced by blanching. However, we



positive reaction. Benzidine gives a more intense coloration than guaiacol; but it also occasionally gives a positive test in the absence of peroxidase, as in a completely cooked sample containing a heat-stable catalyst—e. g., a trace of copper or iron. Potatoes may show a heat-stable catalyst occasionally and will react positively in the absence of enzymes.

Government specifications now call for a negative peroxidase reaction in most dehydrated vegetables submitted for army use.

Blanching in steam is recommended in preference to that in water, since water has been shown to remove large amounts of valuable nutrients from some vegetables (16). Continuous steam blanchers that take the diced or otherwise prepared vegetables directly from the preparation department are used in most plants. Tray blanchers of the batch cabinet type are not desirable because considerable time is required to fill them, allowing enzymic deterioration before blanching; much steam is needed to heat the trays because heating is often imperfect. The continuous blancher consists essentially of a long rectangular wooden or metal box through which a woven wire conveyor carries the prepared vegetables in a shallow layer. Abundant steam must be

> The Center Picture Shows Racks of Dehydrated Potatoes Laid Out in Trays Similar to the Two Shown at the Top; Below Are Several Large Potato Dehydration Tunnels in California

must admit that these undesirable changes also occur, but in lesser degree in the blanched products.

The definite nature of all the enzymes involved in the deterioration of vegetables during dehydration and subse-

quent storage has not been determined. In some cases oxidative enzymes are certainly involved, as in darkening of color and loss of vitamin C. Probably the loss of carotene by oxidation is, at least in part, catalyzed by an enzyme.

Fortunately, for control purposes the adequacy of blanching is readily ascertained by testing for peroxidase or phenolase. Experiments show (9) that for some vegetables blanching merely enough to inactivate catalase but not peroxidase is wholly inadequate to protect against undesirable enzymic changes. Catalase is tested for by placing several small crushed pieces of the vegetable in a test tube, covering with dilute (about 0.01 per cent) hydrogen peroxide, and observing whether or not bubbles of oxygen are released. Peroxidase activity is easily detected either by placing a drop or two of dilute 0.3 per cent hydrogen peroxide and one or two drops of 0.5 per cent guaiacol in 50 per cent alcohol as an indicator on the scarified (scratched) surface of the sample; or by placing several small crushed pieces of the vegetable in a test tube, covering with 5 cc. of water, and adding four or five drops each of 0.3 per cent hydrogen peroxide and a similar amount of the indicator. Of the many oxidase indicators tried (most of them phenolic in nature), guaiacol has proved most dependable. Formation of a brick red or brownish color is a



provided. Frequent peroxidase tests should be made to ensure proper blanching.

Corn should be blanched on the cob for about 15-20 minutes in live steam. Other vegetables take from 3 to 5 minutes (for spinach) to about 15 minutes (string beans). Overblanching results in mushing of the product with consequent slow drying and slablike appearance.

Potatoes should be washed to remove loose starch after dicing or shoestringing and thus to minimize mucilage formation on the cut surface and resultant sticking to the trays. In some cases they require washing in water sprays also after blanching.

Hanes and others in England write that they prefer to "series blanch" the vegetables—that is, blanch successive lots of the vegetable in the same water blanch—and thus build up a considerable concentration of solutes that checks excessive leaching out of valuable nutrients.

FERMENTATION. Shredded cabbage and lettuce mixed with 2.5 per cent sodium chloride and allowed to ferment in special vats give sauerkraut and lettuce kraut, respectively. Both are readily dehydrated after steam blanching for about 10 minutes and are richer in flavor if the juice is also dried. This is readily done by first drying the blanched kraut, placing it in the boiled juice (which it will absorb), and then dehydrating the moistened kraut.

Some other vegetables can also be fermented in the same manner as sauerkraut, then blanched and dehydrated.

BRINE DIPPING. Chace and associates (4) find the vitamin C content of cabbage is better retained if the shredded cabbage is dipped in dilute brine, in cases where considerable time elapses between shredding and blanching.

RCING. A considerable amount of the dehydrated potatoes for army use is precooked in steam and "riced" before drying. This consists in passing them through a special press with perforated end plate which mashes the potatoes and delivers them in spaghetti-like strings on the trays. After drying, riced potatoes can be made into mashed potatoes by heating a short time with milk and a little butter.

Other precooked vegetables can also be riced and dried as outlined for potatoes, and are useful in preparing purées for infant feeding, soups, baked dishes, etc.

#### **Tunnel drying**

**TRAYS.** Wooden, slat-bottom trays,  $3 \times 6$  feet in size, are commonly used in California vegetable dehydrators. Some galvanized iron screen is used for nonacid vegetables.

Monel, nickel, or stainless steel screens are ideal but are unobtainable at present. In some cases the wooden trays should be oiled with slab oil or impregnated with scalding hot paraffin to minimize sticking of such products as onions or blanched cabbage.

Tray loads vary with the vegetable and its state of subdivision; but it usually ranges from 3/4 pound per square foot for leafy vegetables and cabbage to  $1^{1}/_{2}$  pounds for root vegetables.

TUNNELS. Most vegetable dehydrators in the West are of the forced-draft countercurrent type. Carloads of  $6 \times 3$ foot trays loaded with the prepared vegetables enter at the cool end and proceed progressively toward the hot end where drying is completed. Most of these dehydrators were built for and are used in season for prunes or grapes. They are usually 50 feet or more in length and about  $6.25 \times 7$  feet in cross section.

Since vegetables give up their moisture more rapidly than do prunes or grapes and thereby saturate the air more quickly with water vapor, it has been found more efficient to use only 30 to 40 feet of the tunnel for vegetables. If the air becomes too humid, the vegetables merely "stew" and deteriorate in flavor and color without drying; in fact, moisture may condense on them when they first enter the dehydrator in such a case.

The usual finishing temperature is  $140-145^{\circ}$  F. It is often lower for onions and sometimes higher for carrots and beets. Spinach can be dried at  $170-180^{\circ}$  F. in a very short period (about 2 hours) if it is removed as soon as dry. Vegetables (except sweet and white potatoes) are dried to less than 5 per cent moisture (army specification).

PARALLEL, COUNTER, AND MIXED AIR FLOWS. The usual countercurrent system (with air flow in one direction and vegetables moving in the other) was outlined in the preceding section. The vegetables may also progress through the tunnel with the direction of air flow (parallel current system). In this case the vegetables will withstand high temperatures, 200° F. or more in some cases, without injury while high in water content, because they are cooled to wet-bulb temperature, possible below 100° F., by the rapid evaporation of water. As they dry, they progressively approach lower temperatures and increasing humidity, soon reaching a point where evaporation is very slow or may cease.

It then becomes desirable to transfer them to another tunnel or compartment in which the countercurrent system is used. Here the partially dried vegetables travel progressively from a region of moderate temperature and humid-

ity to very low humidity and relatively high finishing temperature, 140-145° F. This is the mixed parallel and countercurrent systems, otherwise known as the center exhaust system. It has been in use in California for a number of years for peppers and pimentos (13). In this case two tunnels are used, side by side. Air enters tunnel 1 at 180° F. and the pimentoes or peppers travel parallel current; they emerge from tunnel 1 partially dried and are transferred to tunnel 2 in which they progress countercurrent from perhaps 120° to a finishing temperature of 150° F.



Battery of Tower Dryers for Apples The third dryer from the left is equipped with air recirculation duct and fan.

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Aitken (2) described this system as used in Canada for apples and vegetables. It has been in use in Nova Scotia for several years for apples and is now in operation for vegetables for the Canadian military forces overseas. He states that six trucks of fresh product of 24 lineal feet of fruit are sufficient to saturate the air "commercially" with water vapor. For this reason the Canadian tunnels hold six trucks in the primary or parallel-current tunnel and four to five in the finishing countercurrent tunnel. In Canada two tunnels may be used or, in some cases, a single tunnel divided near the center by a movable partition. In the latter tunnel hot air enters each end, travels toward the center, and is exhausted from the center-hence the designation "center exhaust system". Walsh (22) states that in England the vegetables travel progressively through five temperature zones during drying-namely, 210-200°, 180-190°, 160-170°, 160°, and 150° F.



Courtesy, E. A. Couture Company Dehydrating Tunnel for Carrots (above); Sorting Dehydrated Carrots to Be Sealed in the 5-Gallon Cans Shown at the Left (below)

HEAT SOURCES. Most dehydrators in California use natural gas as the source of heat. The products of combustion pass through the drying tunnel and in contact with the vegetables or fruit. Heat efficiency, therefore, is high.

Where natural gas is unavailable, the air is heated by passing it over steel flues and a steel boiler shell heated by crude oil or stove oil. In some cases the products of combustion of stove oil heat the air directly. Very few plants use steam heat in this state.

CRITICAL TEMPERATURE. While high in moisture, vegetables withstand quite high temperatures, 180-200° F. or more; but when nearly dry they become quite sensitive to heat. Onions and potatoes often darken at 140-145° F. when nearly dry; carrots, on the other hand, will withstand up to 160° F. when nearly dry.

The deleterious effect is a function of moisture content, time, and temperature. Thus, 3 hours at 140° F. may be

more injurious for dried onions than 150° F. for 30 minutes. Most dehydrators are keenly aware of these facts and take them into account.

FINAL MOISTURE CONTENT. Blanching before dehydration is the most important improvement adopted by dehydrators of vegetables since the first World War. The second great advance is dehydration to a very low water content, for most vegetables below 5 per cent. At low water content, oxidative and other deleterious changes in quality are greatly retarded. Army specifications call for moisture contents below 5 per cent except for potatoes, 7 per cent.

FLAKING. After drying, onions are usually passed through a flaker (revolving rolls that flatten the pieces and break them into lengths). This permits packing a larger weight in each 5-gallon army tin container. The fines are screened out and ground to a powder.

## Other methods of dehydration

VACUUM DEHYDRATION. Drying in vacuum is theoretically an excellent procedure as it makes possible low drying temperatures in the absence of air. According to reports, vegetables and fruits have been dried in vacuo while in the frozen condition at the Low Temperature Experiment Station in Cambridge, England, and elsewhere with remarkable results. But special equipment is required and drying is slow.

The problem in vacuum drying is to transfer sufficient B. t. u. of heat per square foot of tray surface to give a reasonably rapid rate of drying. The equipment is massive and costly. k

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One California company uses fruit and vegetables dried previously in atmospheric dryers or in the sun and then dries them to below one per cent water content in special steamheated vacuum dryers. Apple nuggets (quickly cooked dried apples) are made in this way. Also, some of the vacuum-dried fruits and vegetables are powdered in a hammer mill in an air-conditioned room of low relative humidity and then packed at once in tightly sealed cans. These powdered fruits are useful in bakery products, confectionery, and sauces; the vegetable powders are good for soups, purées, and flavoring.

BIN FINISHING. Two California companies complete the final stages of drying onions and some other products in bins through which air of about 110° F. and low humidity is circulated to dry them to very low moisture content. This procedure prevents heat damage near the end of the drying period, yet permits attainment of low final water content. Silica gel air drying is used at one of these plants to dry the air used for circulation through the finishing bins (5).

DRUM DRYING. In the Sardik process, now in use in New York and recently installed in a California cannery, the puréed vegetables, partially concentrated, are spread on the surface of a highly polished, internally steam-heated, revolving drum, and are dried quickly to an almost anhydrous condition. The dried purée is continuously scraped from the drum as flakes and packed at once in moisture-proof containers. Powdered tomato soups are used by the Army; they are useful for flavoring various dishes. The Buflovak twin-drum dryer is used in one New York plant.

SPRAY DRYING. A plant near San Diego, Calif., has installed equipment for the spray drying of puréed vegetables. Unfortunately the first installation accidentally burned but has been replaced (according to latest accounts). Purées have been dehydrated to powders by other companies, and the procedure is known to be practicable. It should have potential commercial possibilities.

Undoubtedly the addition of a drying agent will be needed in some cases to permit drying of vegetable purées and juices to powders. With fruit juices this is usually dextrose sugar or plain milk. Without such drying agents, fruit juices either fail to dry to a powder and have a gummy sirupy consistency, or are extremely hygroscopic and soon cake from absorbed water. One operator states vegetable purées must be colloid-milled before spraying.

#### Inspection, packaging, and storage

INSPECTION AND REFRESHING TESTS. The Quartermaster Corps and Agricultural Marketing Administration have established specifications for dehydrated vegetables for army use, and the A. M. A. inspects all vegetables for the military and Lend-Lease.

For comparison of our experimental samples, we refresh a weighed amount in a measured volume of water 1-4 hours; determine drained weight; observe texture, color, flavor, and odor; and then cook the samples in beakers by heating them in a steam box until well cooked, usually 5-15 minutes. Comparisons are again made. We score them as follows: Color and appearance, 25; texture, 25; flavor and odor, 50.

WASTE DISPOSAL AND SANITATION. The Agricultural Marketing Administration insists on clean premises, clean equipment, and efficient disposal of wastes. Several plants have been penalized severely for laxity in these respects. The Army also requires cleanliness.

Solid wastes, such as trimmings from carrots, potatoes, and cabbage are useful for stock feed, when fed with more solid feeds such as hay and grain. Starch can be recovered from the aqueous effluent from mechanical potato peelers. Wash waters must be disposed of by suitable sewage disposal plants; running such waters into open fields has resulted in obnoxious odors and temporary closing of the plants as public nuisances.

However, that era seems to have passed and operators are now doing their best to maintain clean plants and to dispose of wastes in accordance with board of health requirements.

PACKAGING AND STORAGE. As one army officer put it, "Dehydrated foods must be packed for army use in such a manner that the package can be thrown overboard into the sea by a landing party of soldiers in the South Seas, float it in through the surf, carry it ashore, and store it there in a driving rain in the rat-infested jungle without danger of spoilage or loss." That is a large order!

Hermetically sealed metal containers are therefore usually specified by the Army. The usual container is a 5-gallon rectangular can. The lid is sealed either with solder or with a double seamer after being filled with the dehydrated product. Two cans are packed to each wooden case.

Bags of laminated paper, asphalt, plastic film, and lead foil have been suggested, but certain insects such as the cable borer beetle can easily chew their way into such bags and rodents can also break into them. Probably heavy aluminum foil bags, heat-sealed, would be satisfactory.

The package must prevent pickup of moisture from the air, or deterioration will be very rapid.

CODING. It is very desirable to code all packages of dehydrated vegetables with variety, date when packed, and shift (day or night) when packed in order that causes of spoilage or rejection by federal inspectors may be traced and defective lots easily segregated.

VITAMIN LOSSES. During the past year Mackinney, Aronoff, and Sugihara of this laboratory have studied the losses in carotene and vitamin C during dehydration and subsequent storage. In blanched vegetables the loss in C is much less during drying than in the unblanched vegetables; but in subsequent storage its loss is rapid, even in the blanched dried products.

 $\beta$ -Carotene (precursor of vitamin A) decreased rapidly in dried carrots stored in air but much more rapidly in the unblanched than in the blanched condition. The unblanched carrots became practically white in 2-3 months at room temperature. Stored in nitrogen or carbon dioxide, the rates of loss were much less. Loss was also slow in cold storage in air at 32-36° F.

In Canada cans of dried vegetables for army use are evacuated in a vacuum chamber and then filled with nitrogen or carbon dioxide. In the United States vacuumizing is omitted; carbon dioxide is run into the bottom of the filled container until the gas flowing out of the can will extinguish a match. Probably a large amount of oxygen remains in the package, but the atmosphere is probably much less oxidative than plain air; also the carbon dioxide should prevent hatching of any insect eggs that may occasionally be present.

Unpublished studies by Mackinney, Morgan, Sugihara, and others at this university and by various other investigators indicate that vitamins  $B_1$ , G (riboflavin), and nicotinic acid are quite stable to dehydration unless sulfur dioxide is used; in that case  $B_1$  is damaged or destroyed (21).

INSECT CONTROL. Insects are irresistably attracted by dehydrated vegetables and fruits, although at moisture contents below 5 per cent insects are much less apt to develop in dried vegetables.

Fumigation of stored dried fruits with methyl bromide at regular intervals of 3 to 4 weeks is regular practice in California dried-fruit packing plants. As yet, dried vegetables generally are not fumigated; they are taken off the trays when they come from the dehydrator and packed at once into carbon dioxide filled, hermetically sealed cans. Soup-mix



Top. Cutting Fruit for Drying in Farm Dehydration Center. Sun Drying Peaches in California Bottom. Dehydrated Pears

vegetables for civilian use are packed into tight-sealed insectproof drums, shipped to the packaging plant, and there packed in insect-proof packages. If they are to be stored in bulk, they should be fumigated with methyl bromide or other modern fumigant. Hydrogen cyanide leaves a residue of prussic acid, carbon disulfide is very explosive, and most other fumigants are not efficient. Methyl bromide is rapidly displacing other fumigants for this purpose.

However, ethylene oxide and ethylene dichloride are often added in mixture as a liquid (a few cubic centimeters to each box of dried fruit at time of packing). This is effective and can also be used for dried vegetables.

Heat can be used to destroy insects in dried vegetables for example, by heating them on trays in the dehydrator at 140° F. for an hour or two and then packing at once in insectfree insect-proof packages.

### **Control analyses**

The moisture content of dehydrated vegetables must be determined regularly since physical appearance and texture are not dependable guides. Drying in vacuum oven to constant weight by the A. O. A. C. procedure is the accepted reference method. Drying a previously determined time at 100° C. at atmospheric pressure or at very high temperature (250-275° F.) for a very short time (10-15 minutes) are also in use. Our tests indicate that distillation of a 25or 30-gram sample in a 50:50 mixture of toluene and xylene for a specified time and measuring the volume of the water distillate is fairly satisfactory. Xylene alone gives erratic and high results, owing to its too high boiling point, and toluene gives too slow a rate of distillation owing to its too low boiling point.

Electrical instruments based on conductivity of the sample or on its electrical capacitance are under study and may be adopted eventually. They are now in use for dried fruits and cereal products, respectively. Aitken (1) recently described a simple inexpensive set-up for quickly determining moisture in dehydrated vegetables in vacuo.

Vitamin C determination by titration with dichlorophenol-indophenol solution of a sample whipped up in dilute phosphoric acid solution in a Waring Blendor is used successfully in several laboratories. Carotene can be determined by extraction in suitable solvent, separation in a Tswett column, resolution, and reading in a spectrophotometer or special colorimeter; but its successful determination requires considerable experience and training. Determination of the other vitamins is too slow and difficult for most commercial dehydration laboratories.

#### **Rehydration and use**

DEHYDRATION AND REHYDRATION RATIOS. In a recent article Logan (15) gave approximate average dehydration and rehydration ratios for several vegetables (Table I). The values for rehydration are especially useful; dehydration ratios vary greatly according to the raw material used.

#### Table I. Dehydration and Rehydration Ratios (15)

Dehydrated Item	Dehydration Ratio	Rehydration Ratio <sup>a</sup>
Beets	10:1	1:7
Cabbage	18.5:1	1:8.50
Carrots	10:1	1:5.75
Onions	10:1	1:6
Potatoes, sweet	4:1	1:3
Potatoes, white riced	6:1	1:5
Potatoes, white Julienne	6:1	1:3.67
Turnips, vellow	12:1	1:6
Apple nuggets	10:1	1:8
Cranberries	10:1	1:12 (sauce)
Eggs, whole		1:3.30
Milk, skim	11:1	1:10
Soup, pea or navy bean		1:4 thick, 1:6 thin

<sup>a</sup> Pounds prepared for the table from 1 pound dry.

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	Dehydra- tion	No Prel Treat	imin <b>a</b> ry ment	Soal Overn	ked hight	No Prel Treat	iminary ment	Soal Overi	ked night
Vegetable	Ratio, Blanched	Time to cook, min.	Recovery ratio	Time to cook, min.	Recovery ratio	Time to cook, min.	Recovery ratio	Time to cook, min.	Recovery ratio
arrots	10.0	15	4.2	10	6.9	30	4.6	30	6.5
otatoes	5.6	20	3.7	10	4.0	40	3.2	a	
ninach	9.6	10	5.4	10	5.7	10	5.2	10	6.7
abhage	14.9	15	7.0	10	9.2	20	7.7	ь	
Pas	4.3	30	3.6	20	4.0	a		с	
string heans	9.7	10	5.8	- 5	7 6	-		a	
ima beans	3.2	15	3.2	10	3 3	40	3.8	40	3.4
Leets	11.7	15	4.2				0.0		
lorn	4.6	10	3.0			20	3 1		
ucchini squash	16.5	10	4 2			10	4 6		
ummer squash	12 1	10	3 6			10	4 0		
auliflower	12 7	10	4 7			b	1.0		
aunower	10.0	10	6.7			30	7 9		
augebreut	17 3	10	6.0			10	5.0		
lumpking	11 0	10	5.0			10	4.2		
Therd	12 6	15	6.0			20	4 8		
	0.6	10	3 4			10	2 2		
	0.0	10	0.9	••		20	4.0		
rarsmps						20	*2.0	* *	
Not cooked in Not cooked in Not cooked in	40 min. 30 min. 20 min.								

In experiments on the effect of blanching on dehydration, Sugihara and Cruess made the observations on dehydration and rehydration ratios listed in Table II. Comparison of Tables I and II shows that drying ratios and refreshing and cooking ratios may vary considerably for a given vegetable.

SERVING. Logan (15) gives the following schedule for serving dehydrated vegetables to soldiers, both in the United States and overseas; enough servings are made to soldiers here to acquaint mess personnel with preparing, refreshing, and cooking the dehydrated vegetables and to test the soldiers' reaction to them:

	Ounces per M	an per Serving	No. Servings	per Month
Item	Dry	Cooked	Domestic	Overseas
Potatoes	1.44	5.3	1	12
Onions, sliced	0.66	4.0	1	6
Cabbage	0.624	5.3	1	6
Potatoes, sweet	1.33	4.0	1	6
Carrota	0.557	3.2	1	3
Beeta	0.47	3.2	1	3
Rutabagas	0.53	3.2	Ó	3

On the basis of such data, estimates can be made of the tonnage of dehydrated vegetables needed for overseas units.

#### **Dehydration** of fruit

This paper has dealt chiefly with the dehydration of vegetables. The dehydration of fruits has been well covered (5, 7, 19) in other publications.

Recently Mrak and Phaff (18) devised a new and improved method of preparing cut stone fruits and pears for dehydration. When sulfured in the usual manner for sun drying and then dehydrated, these fruits yield chalky or opaque dried products that are unacceptable in appearance to the trade. Mrak and Phaff find that, if these fruits are thoroughly steamed before sulfuring, they yield translucent dehydrated products of excellent commercial quality and acceptable to the trade.

At present practically all dried apricots, pears, and unbleached raisins are dried in the sun. More than half the prunes are also dried in the sun. Most cling peaches that are dried (the amount is not great) are dehydrated after preliminary sulfuring. Apples are dehydrated.

Mrak, Friar, and Phaff have found that berries can be dehydrated successfully if bleeding is avoided during initial stages of drying. Light sulfuring in sulfur dioxide fumes is desirable.

Cruess (8) found that peaches and apricots yield fairly satisfactory products if merely well blanched in steam or in hot sirup before dehydration. Prunes steam-blanched before dehydration give a dried product that, on cooking, closely resembles cooked fresh prunes in color and flavor. The customary dried prune has dark flesh and oxidized flavor; the steam-blanched dehydrated prune is pink in color and has a fruity flavor. Mention has been made of the production of dried fruit "nuggets" and powders by redrying previously dried fruit to very low moisture content in vacuum drvers.

Cruess and Sugihara (11) found that sliced citrus fruits can be dehydrated readily, with or without preliminary sulfuring, and still retain most of their vitamin C. They are very satisfactory for making marmalade and hence can be exported to England for that purpose with great saving in cargo space and without need of refrigeration.

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# Conservation of perishables by refrigeration

M. E. PENNINGTON, 233 Broadway, New York, N. Y.

• • Public and private refrigerated space is strained to the utmost, and good planning and the cooperation of all are needed. Civilians must look forward to fewer cans and jars and more frozen perishables in packages.

Frozen food locker plants, now in existence, are carrying an estimated half billion pounds of food locally produced and consumed. They can carry more. They reduce labor, transportation, and distribution costs and conserve food at the source. Farm freezers do likewise. They are now under a priority requirement of A-9, but the more of them we have on the farms, the less trouble we shall have feeding our farm folk.

Refrigerated space on our merchantmen is too little to hold enough food for the long voyages required by war conditions. The temperatures are inadequate for the preservation of perishables in a palatable condition for more than a few weeks.

Food conditions in the United States will not return to normal as soon as the guns stop firing. The Americas must then send food to victors and vanquished as well as every sort of peacetime supply. The conservation of perishables and their distribution is a problem for the future as well as the present.

T NO TIME in history has the conservation of food, especially perishable food, been of greater importance than in this World War. Normally, we in the United States would depend upon canning, dehydrating, and freezing, as well as on salting, curing, and smoking. Refrigerated railway cars and motor trucks and steamships would transport the cooled or frozen products to the desired destination where, nine times out of ten, a refrigerated warehouse would await them. Our American dietary, rapidly expanding in quality and variety as vitamins, calcium salts, phosphoproteins, etc., have become household words, has been held in jars, cans, locker freezers, and bins in whatever form most appealed to the prospective consumer. Food conservation has been based on the saving of a normal surplus production, on an even distribution of seasonal products throughout the year, and a leveling of prices-all from the viewpoint of American requirements and preferences.

Now under the conditions of total war, with our soldiers on the shores of the seven seas and our sailors on their waters, the problem becomes entirely different. In addition to feeding our troops abroad and at home, we must feed our allies. They are far flung. China needs milk for its motherless children. Russia needs fats for its people in the north. Great Britain needs a wide variety of foodstuffs. When the guns stop firing and the restraints of active war are somewhat removed from the people of conquered nations, the cry for food, food, and more food must be heeded promptly.

The relatively small amount of metal available for cans must be held for supplies to the Army, Navy, Merchant Marine, and our allies, such as evaporated milk and meat products. In July, 1942, Lend-Lease purchases of frozen pork amounted to some 8,000,000 pounds, but canned pork reached over 132,000,000 pounds. There will be practically no cans for civilians. Our young food-dehydrating industry, though growing by leaps and bounds, as yet falls far short of the quantities of vegetables required for oversea use. Civilian needs everywhere are now secondary to those of the armed forces. Civilian needs here in America must be satisfied with what food is available. Thanks to starting the upward push of production more than two years ago, we are likely to have enough for civilian needs (not luxuries), provided we conserve efficiently what is produced and distribute evenly as the demand arises.

At present we have only one method (low temperatures) by which we can preserve the characteristics of what we term "freshness" in perishable foods—flavor, color, appearance, and texture. Not necessarily freezing temperatures, because such staples as apples and eggs are held from season to season at 29° to 31° F. Nevertheless, more and more products under a wider and wider variety of conditions are being conserved by freezer storage and the approved temperatures have dropped lower and lower.

To the limit of the carrying capacity of the allied refrigerated ships, we will send overseas for fighting men and for civilians frozen meat, butter, eggs, poultry, and edible fats. But the shipping capacity falls far short of the tonnage required. Neither will we find refrigerated warehouses at all debarkation points to carry safely the frozen perishables until distribution is accomplished.

Yet for Lend-Lease, at this writing we have already purchased more than 500,000,000 pounds of perishables which must be transported and held under refrigeration. Europe has never used refrigerating temperatures so low or so universally as has America. In the first World War we sent our engineers to France ahead of the supply ships to build refrigerated warehouses at the ports where frozen food could be safely held. The lack of such efficiently refrigerated space in England has been a handicap on the ultimate quality of food sent over in this war. It is easy to see, then, why the meager available stock of steel plate and tin must be kept for essential products to go overseas and why art, science, and American resourcefulness are working overtime to produce more and better dehydrated products. In large measure they, too, must go overseas. Meanwhile, civilians in this country must also be fed.

According to a survey made by the United Stated Department of Agriculture in 1941, we have in this country a total of about 766,000,000 cubic feet of refrigerated space. This includes public and private cold storage warehouses and meat packing plants. More and more commodities are being held in freezers at 0° F. and below, instead of coolers at 30° F. and above. Instead of 60 per cent cooler and 40 per cent freezer a in

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space, we now turn the figures around. Officials in Washington, making plans and solving problems concerning refrigerated space, expected that by October, 1942, the freezers of the country would have over 1,257,000,000 pounds of pork, fruits, vegetables, butter, and frozen eggs, to be further increased in December by over 300,000,000 pounds of poultry and meats. We now have 9,600,000 cases of eggs in cooler space.

Much of this tonnage is en route to steamers to be shipped Lend-Lease or to our own bases outside the continental United States, and only waits in warehouses for sailings. Even so, occupancy now of cold storage warehouses is reported over 70 per cent, while packers and private facilities are at 90 per cent or over. Hence, on all accounts, we are looking as never before at the size of packages and the saving of space. For example, one ton of carcass beef will occupy 135 cubic feet of space, be it hung or piled. Deboned and packed into cartons, it will occupy 36 cubic feet. A crate of fresh spinach, holding 41 pounds, occupies 2.8 cubic feet. Blanched and frozen, a package of spinach holding 40 pounds occupies 1.11 cubic feet.

Space in cars and trucks, whether refrigerated or not, is at a premium. Some products take less space frozen and weigh less than when canned. For example, a million pounds of peas frozen in 12-ounce cartons require 27,940 cubic feet of storage space, while in 2-pound cans they need 43,180 cubic feet. To move the frozen peas would require thirty-one carloads of 36,000 pounds minimum. The canned peas would need sixty-four carloads.

#### **Quick freezing**

The refrigeration of perishables grew, as do so many American projects, rather like Topsy. The cut-and-try method could go just so far. In 1903 the United States Department of Agriculture sent its young scientific men to study the conservation of peaches in Georgia; and in 1905 the department began its studies of conservation of poultry, eggs, and fish. Milk and butter were already receiving scientific attention.

It was not until well into the twenties that the refrigerating industry in the United States began to look with a commer-



Courtesy, Refrigerating Engineering

Fruit Stored in a Cold Storage Room



Courtesy, Refrigerating Engineering Typical Cooler Room in a Locker Plant

cially appraising eye at the facts coming by the scientific route. Two facts were outstanding—the enthusiastic reception by the householder of the mechanically operated refrigerator and the results as demonstrated by Birdseye of the quick freeze. When a hostess served quick frozen foods to her guests and told them how she could keep a supply in the freezer compartment of her refrigerator, the food purveyor dared no longer malign frozen foods as "cold storage stuff", and the refrigerated warehouseman seriously set about harmonizing the temperatures and conditions in his warehouse with the findings coming from the laboratories.

The definition of "quick frozen" has undergone several modifications since its use became general. As originally defined, it signified passing through the zone of water crystallization—that is, from  $+31^{\circ}$  to  $+23^{\circ}$  F.—in not more than

30 minutes. Crystals formed with such speed are extremely small. They are intracellular, and on thawing, the water is more readily absorbed by the cellular substance. Such speedy freezing was difficult, even for small packages. It was almost impossible, commercially speaking, for packages weighing 20 or 30 pounds such as are needed for institutional and quantity serving.

Uniformly fine quality goods in packages of family size, on the one hand, and institutional size, on the other, were the goals to be obtained. One packer used a tunnel machine and put an acceptable product on the market. Another used low-temperature metal plates against his packages, and the contents froze satisfactorily. Another spread out his pack in a room running  $-25^{\circ}$  F. and kept the air circulating, and his product found favor in the sight of the customer, and so on.

The classical researches of Plank (1) showing the percentage of water frozen out of meat at different temperatures with a total freezing at  $-67^{\circ}$  F. and some denaturing of the protein caused considerable scientific consternation but not much practically. It was too difficult to obtain such extremely low temperatures commercially, and time did not permit holding packages in the quick freezer for such lengthy periods.

Now, a dozen years since we discussed by the hour the method of getting a 30-minute water crystal freeze so that we might call the product "quick frozen", we have adopted the term for any package of household or institutional size containing a food product hard frozen in a form ready for cooking or serving. If the quality is consistently good, the consumer asks no questions about how long it took to freeze the contents.

It is to refrigeration, particularly freezer preservation, that our civilian population, especially, must look for an even apportioning of perishable foods throughout the year. Fresh fruits and vegetables in season will be marketed in larger quantities since canners and jam and jelly makers must be restricted in the use of tin and sugar. So far we have had enough refrigerated cars and trucks to haul the fresh goods. Fortunately, frozen goods can be held in fiber containers, provided they are moisture vapor resistant. Desiccation is a bitter foe of quality in refrigerated perishables.

We put up approximately 40 per cent more quick frozen package goods in 1942 than in 1941. Some of it went to the Army where it has been tried and found useful for United States camps. Much more has gone to the Navy which, since 1936, has put some 0° F. carrying space in all new ships and in those overhauled and refitted, and so can hold frozen foods successfully. Next year the Army will want more quick frozen perishables, and civilians will have far fewer cans. The aim, therefore, is to double the 1942 quick frozen pack in 1943.

Considerable planning must go into such a program. In the first place, not all varieties of vegetables and fruits will freeze successfully. Therefore, the farmers must agree to plant varieties of peas, beans, beets, and so on, which are suitable for freezing. The freezing facilities now available can be pushed to give a larger output, but they cannot double our

present plant capacity. Relatively little new steel would be required, considering the tonnage to be obtained, but steel is steel and every pound counts.

It is estimated that forty thousand grocery stores are selling frozen foods direct to consumers. The volume sold in 1942 increased greatly over 1941, but the business they can do, using the cabinets they now have, could be much heavier. If their facilities should give out, every ice cream shop could be a distribution point for the dinner as well as the dessert.

There is a new development in the offing--namely, frozen cooked foods. Our old friend, pork and beans, banished from the can by the exigencies of war, now appears frozen in a paper carton. It is only a question of time until spaghetti in tomato sauce, corned beef hash, and other stand-bys fall back upon quick freezing and paper containers.

#### Locker plants

A development of significance, especially in view of civilian food conservation during the war, is the frozen food locker plant. Here in large rooms, held at  $0^{\circ}$  F. or below, are lockers, generally built of steel in the form of stacks of drawers, five high, each drawer having a capacity of about 6 cubic feet. Each locker will hold from 150 to 250 pounds of meat or fruits or vegetables. There are now more than 4500 locker plants in this country, in which the owner of the goods has direct access to his frozen produce. There is an average of 350 lockers per plant, which means that a million and a half farm families can conserve food by locker freezing. Assuming five persons to a family gives a total of nearly 8,000,000 people who may be so fed.

Usually the locker plant also provides facilities for cooling and ripening meat, cutting carcasses, and wrapping in household size packages, a workroom where fruits and vegetables are prepared and packaged for freezing, and a sharp freezer where the initial freezing is done. The frozen goods are then transferred to the customer's locker, to be removed as he desires.

Many an ice making plant has converted some of its ice holding space into locker rooms, and many a cold storage warehouse has diversified its business by adding lockers.

Locker plants began as a convenience for the rural population. Now urban populations, especially of the smaller cities of the Midwest, have also adopted this method of conserving perishables. In 1941 the tonnage so held was estimated at more than 500,000,000 pounds. With the present scarcity of tin for cans and of all metals suitable for tops of jars and of rubber for closures, it is probable that we will see a big increase in the quantity of civilian food stored in locker plants.

Cabinets in a Frozen Food Locker Plant



#### January, 1943



Courtesy, Refrigerating Engineering

A Meat Cutting Room in a Frozen Food Locker Plant

locker conditions, and much valuable information has resulted. The conclusions are that vegetables and fruits, if stored at temperatures above 0° F., lose their color, flavor, and vitamin C content. Meats require 0° F. or lower. The higher the temperature, the sooner the fat becomes rancid and objectionable flavors in the meat develop. Pork is the most sensitive. It becomes rancid in 2 months at 15° F. and in four months at 10° F.; but at 0° F. there is no sign of rancidity at the end of a year. Beef, lamb, and veal are more stable, but show signs of rancidity in the fat at the end of 3 months at 15° F. and of 5 months at 10° F. At 0° F. they are free from rancidity at the end of 12 months.

Frozen food locker plants are a great asset in the feeding of

civilians. Scattered in rural communities in every state, easily accessible, and, in general, efficiently refrigerated, they constitute a food bank which is capable of far wider usefulness as the pinch of a civilian food supply develops and the necessity for the conservation of every pound of food produced becomes apparent. Already some locker plants are acting as exchanges where the surplus from one farm and shortages on another can be equalized. Occasionally a locker plant does a merchandising business in frozen foods and there are potential possibilities in this direction should our 40,000 retailers be insufficient.

#### **Refrigeration of ships stores**

The war emergency found us with land-based refrigerating facilities and processes sufficiently flexible to permit their utilization as necessity indicates and, with good planning, fairly adequate for the work to be done. But the job to be done on the seas is new, and for the exigencies of the present situation we have at least one outstanding lack—namely, refrigeration for the preservation of ships stores. Our merchantmen carrying supplies to troops and to our allies must frequently provision for a round trip of six months. During that time the only food to be depended upon is that supplied the ship before it left the United States port.

The old days have gone by when salt pork, canned potatoes, and dried apples were the menu for the ship's crew. Now the men must have a balanced American diet with fresh meats and poultry, vegetables and fruits, eggs for breakfast, fresh milk as long as possible, ice cream and newly baked cakes, and an abundance of fruit juices to ensure against scurvy. Recent studies of dietaries state that a sailor in our Navy consumes 1985 pounds of food per year, a soldier, 1844 pounds; while a sailor in the Merchant Marine requires 2555 pounds or about 7 pounds per day. Given a wartime crew which is ordinarily increased from 30 to 60 per cent, the problem of space in which to stow sufficient food becomes

#### Farm freezers

In addition to locker freezers for public use, cabinets with self-contained freezing units have been manufactured and termed "farm freezers". They range in capacity from 10 to 30 cubic feet, are provided with a small refrigerating machine capable of reducing the temperature of part of the space to  $-10^{\circ}$  F. and of holding the remainder at 0° F. or a little above, and are generally operated on motors of 1/4 to 1 horsepower. These farm freezers were just becoming popular when their production was discontinued for the duration. However, enough of them have been distributed to show that they are practical and economical and, in the present emergency, highly desirable for farm homes.

Aside from the conservation of tons of perishable foods, the locker plants and farm freezers have led to a much wider knowledge, especially on the part of housewives, of fruits, vegetables, and the cuts and kinds of meats. The quick frozen industry pioneered in the study of the kinds of produce to grow for freezing. Seedsmen have become familiar with the varieties of fruits and vegetables that will freeze satisfactorily, and can advise customers wisely. Home demonstration agents and county agents are ready and able to expound and explain conservation by freezing. Locker plants have printed and distributed, free of charge, booklets giving instructions for preparing goods for freezing. State experiment stations have published excellent bulletins based on the research work of their own staffs. Altogether, the many educational agencies have transferred a large section of the public mind from an ignorant prejudice against frozen foods to an enthusiastic acceptance of them.

In the early days very few lockers kept temperatures steadily below  $+10^{\circ}$  F. and almost none maintained  $0^{\circ}$  F. Consequently the products spoiled. As a result, condemnation of the whole project was widespread. State food authorities then took a hand in the proceedings and issued instructions and orders. State experiment stations instituted research based on the preservation of perishables under 65

extreme, quite aside from preserving it in palatable condition. No one who has ever gone down to the sea in ships can begrudge the crews good food, as Americans know good foods, and the ship operators are going to every length to provide an excellent and attractive dietary.

But while fruit shippers and meat packers, knowing the refrigeration requirements of their commodities, have cooperated with shipbuilders in the refrigeration of cargo space, apparently no one has applied the universally accepted temperatures for food preservation to the space for carrying ships stores.

Rohn and Clarke (4) state that in the new cargo ships the service compartment for meat carries a temperature of 22° to 26° F. Fish is kept at 20° F. and dairy products at 45° to 50° F. In passenger and cargo ships the temperatures in the freezer compartments range from 15° to 20° F., butter and eggs at 40° to 45° F., and ice and ice cream at 20° to 25° F. The established preservation temperatures (3) for these commodities are: meats  $0^{\circ}$  F. and below, fish  $0^{\circ}$  to  $-10^{\circ}$ , ice cream 0° to  $-20^{\circ}$ , butter 0° to  $-20^{\circ}$ , and eggs in the shell  $+29^{\circ}$  to  $31^{\circ}$  F. Such being the facts, we may expect eggs in ships stores to rot, butter to become rancid, and meat and poultry to develop rancidity and off-flavors, assuming the voyage lasts for more than a few weeks.

Tressler (5) reports undesirable rancidity in pork in 2 months at 15° F., "while beef, lamb, veal, and chickens become unpleasantly rancid in three months when held at +15° F.". In addition, the products held at 10° to 15° F. develop unpleasant flavors. At 22° to 26° F. deterioration will progress even more rapidly. Canned goods are used as far

as possible and dehydrated foods are increasing, but in these days fresh foods must form a portion of the ration. Quick frozen foods for ships stores, so far as space and weight saving are concerned, are ideal, but they must be held at 0° F. or lower.

The temperatures given by Rohn and Clarke have been bequeathed to our merchantmen by the European shipbuilders. They are the temperatures in use in Great Britain and on the Continent, neither of which uses low temperatures for storage in the American sense of the art. According to Raymond (2), the newest refrigerated warehouses built in Great Britain during the war have gotten temperatures down to 14° F., still much too high but better than the 23° to 26° F. which did prevail.

When the high seas were free, the ship's operator might in various ways compensate for the lack of preservation temperatures. Now his restricted refrigerated space must act as a cold storage warehouse for six months, a considerably longer time than the average period in land warehouses. It would seem imperative that attention be given at once to the conservation of food for crew and passengers aboard ship under present conditions.

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# Enrichment of flour and bakery products

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• • • The enrichment program for flour and bakery products is outlined briefly. Standards and their significance for each are discussed.

Standards for enriched flour have been promulgated and the flour industry has a definite legal status which it follows. However, the baking industry is still working under standards proposed by the Committee on Food and Nutrition of the National Research Council. Even under these makeshift conditions, a large percentage of the family flour now being sold is enriched, and approximately 65 per cent of the white bread sold in the United States today is enriched. The use of these products by the armed forces is discussed; the Army is using enriched flour.

Certain flours are enriched by special milling processes. Such products are compared with those enriched with synthetic vitamins.

THE fortification of food products has been made possible as a result of the investigation, isolation, and syntheses of vitamins. Many of these essential vitamins (and also minerals) can now be added economically to our common foods. The fortification of products with certain of these nutrients has been practiced for several years. However, most of the fortified products have not been a part of any national program whereby the welfare of the Nation as a whole would be benefited. Most of the products fortified have been those that are not generally used by people in the low income brackets, either because of preference or because

of cost. Any program that is to give these nutrients to the ones that need them most must add them to a universally used, economical product.

Before the present enrichment program was made effective, the addition of potassium iodide to table salt stood alone as a sole example of the addition of a nutrient to a food used universally. The selection of bread and flour as the medium for bringing these benefits to the whole population has given considerable impetus to such a program.

Since 1932 vitamin D fluid milks have been produced by direct irradiation of the milk and by the addition of concentrates of vitamin D (31). Although the sale of such milk has reached a large volume, in most localities it still costs more than the regular milk and thus does not reach the lower income classes. However, the bulk of the canned evaporated milk produced for domestic use has been fortified with vitamin D in such quantity that the total vitamin D content is not less than 7.5 U.S. P. units per ounce of finished milk (13), and is available at little, if any, additional cost to the consumer. Fortification of the latter kind of milk has probably been of more benefit to the lower income classes than the former.

The addition of vitamin A to margarine has been in effect from two to three years. In the standards of identity for oleomargarine (15), vitamin A is included as an optional ingredient, and can be added as fish liver oil or as a concentrate of vitamin A from fish liver oil. If it is included, however, it is to be present in such quantity that the finished oleomargarine contains not less than 9000 U.S.P. units of vitamin A per pound. These standards became effective in June, 1941. Within the last year the majority of manufacturers have added vitamin A to their margarine. This figure has increased to the point where practically all of the margarine sold has vitamin A added.

#### Enriched flour and bread

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A white bread was produced as early as 1923 that contained the vitamins and minerals considered significant at that time (21). The first fortified bread met with commercial failure, undoubtedly because the general public did not understand the need for such nutrients; even today the enriched program outlined below is doomed to failure unless the people are educated to appreciate the nutritive value of enriched over unenriched bread. In fact, in the present program a few bakers have already done more harm than help through their advertising.

The development of the enrichment program up to April, 1941, was given by Tobey and Cathcart (32). Therefore, most of the earlier developments will be mentioned only briefly.

In recent years it has been proved that certain important vitamins and minerals that are natural to wheat are greatly

Enrichment Tablets Being Added to an Emulsifier

Which Will Disperse Them in Water and Feed Them Direct to the Dough Mixer

reduced in the process of milling flour. At a symposium on the fortification of foods, held at the meeting of the American Institute of Nutrition in Toronto in 1939, it was recommended that consideration be given to the restoration of these nutrients to refined flour and white bread (3). This was finally crystallized at hearings on proposed flour standards under the Federal Food, Drug, and Cosmetic Act in 1940, and on proposed bread standards in 1941. The flour standards have been promulgated (14) and include a standard of identity for "enriched flour". The quantities of vitamins and minerals allowed under enriched flour are given in Table I.

Table I. Standards for Enriched Flou	e .
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	Minimum	Maximum
Required ingredients, mg./lb. Thismine Niacin Riboflavin <sup>a</sup> Iron	1.66 6.00 1.20 6.00	2.50 24.00 1.80 24.00
Optional ingredients Calcium, mg./lb. Vitamin D, U. S. P. units <sup>a</sup> Requirement postponed until April 2	500.0 250.0 20, 19 <b>4</b> 3.	2000.0 1000.0

Although riboflavin appears in the standard as a required ingredient, due to the shortage of supply, the effective date for its inclusion has been postponed until April 20, 1943 (17). Standards of identity for enriched bread have not been finally promulgated (August, 1942). Enriched bread, how-

ever, is being produced on the bases and recommendations of the Committee on Foods and Nutrition of the National Research Council. These recommendations were made after meetings with the milling and baking industries. The proposed standards for enriched bread as given in Table II are

Table II. Proposed Stand According to Committee on National Resea	ards for Enriche on Foods and Nu arch Council	d Bread trition,
	Minimum	Maximum
Required ingredient, mg./lb. Thiamine Niscin Iron	1.0 4.0 4.0	4.0 16.0 16.0
Optional ingredients Riboflavin, mg./lb. Calcium, mg./lb.	0.8 333.0 160.0	3.2 1333.0 640.0

essentially as set forth in the proposed standards of identity for enriched bread by the Federal Security Agency (16). The only essential difference is that the Food and Drug Administration of the Federal Security Agency proposed that riboflavin be a required ingredient. The Committee on Food and Nutrition of the National Research Council did not recommend it as a required ingredient. Riboflavin is not included at the present time in enriched bread because of insufficient supplies.

Slight changes in the enriched bread standards were proposed by the National Research Council during the Bread Hearing in 1941, and the new proposed standards are given in Table III. The final standards, however, have not been promulgated, and it is not known whether changes will be adopted. These standards are more desirable than the ones being followed at present due to the fact that the minimum values are approximately minimum whole wheat bread levels. However, some enriched bread now on the market meets these requirements. All the standards so far have been based on a process of restoration and not fortification.





Modern Mixer Which Will Mix 1200 Pounds of Bread Dough and Is Equipped with Safety Devices, Water-Cooling Jackets, and Timing Devices

It is desirable that some changes be made in the final standards of identity for enriched bread, and that the standards of identity for enriched flour be changed in the future. There are two reasons for this: The minimum standards of identity for enriched bread as they stand now do not produce bread that is entirely equivalent to whole wheat bread with respect to the required nutrients (except riboflavin); and enriched bread in regard to thiamine cannot be produced by using enriched flour-that is, enriched flour that contains the minimum of thiamine (1.66 mg. per pound) will seldom produce white bread that will have 1 mg. of thiamine per pound in the finished loaf. This is due to the fact that losses in thiamine in baking were not properly taken into consideration when correlating the two standards. Also, enriched bread containing the minimum of niacin and iron can barely be made from enriched flour containing the minimum of niacin and iron. Thus the margin of safety allowed is small. This is one reason why few, if any, commercial bakers are making enriched bread from enriched flour.

Table III. Proposed Chang Bread as Given	ged Standards for at Hearing, 1941	Enriched
	Minimum	Maximum
Required ingredients, mg./lb.	1 1	0.0
Mineir	1.1	4.4
Dibeferin	10.0	20.0
AIDONEVIN T	0.0	1.2
Iron	8.0	10.0
Optional ingredients		
Calcium, mg./lb.	300.0	1200.0
Vitamin D. U. S. P. units	150.0	600.0
from a of ot of a date	100.0	000.0

#### Comparison of enriched with whole wheat bread

The vitamin and mineral contents of whole wheat and the bread made from it vary greatly. In general, the hard spring wheat varieties are higher in these nutrients than other varieties; however, there are also differences in single strains of wheat (9, 12, 28). The thiamine content of 100 per cent whole wheat bread will show on the average about 1.35 mg. per pound (6, 7, 22, 33).

The niacin content of whole wheat bread varies between 10 and 16 mg. per pound. The average is probably near 12 mg. (1, 6, 11, 30).

The iron content of whole wheat bread shows considerable variation. However, the average is close to 10 mg. per pound (6, 18, 24).

The amount of riboflavin in whole wheat bread averages approximately 0.55 mg. per pound, although here again considerable variation is shown (4, 11).

Comparing these figures for whole wheat bread with the minimum standards being followed (Table II) shows that in all respects except riboflavin content the minimum requirements for enriched bread do not come up to the whole wheat bread level. The proposed standards as given in Table III are more nearly in accord with whole wheat bread levels, and it is to be hoped they will be promulgated.

There are other vitamins and minerals in whole wheat than those included in the enriched bread standards. The vitamins are mainly members of the B complex group; those known at present are  $B_6$ , pantothenic acid, choline, biotin, inositol, and factor U. Little is known about most of these vitamins. However, present information as outlined by

Elvehjem (10) shows that the losses of vitamin B<sub>6</sub>, pantothenic acid, and choline are very small in the process of converting whole wheat to white flour. Insufficient data on biotin indicate that loss of it may be great. No data are available on inositol and factor U. Thus, most known vitamins of whole wheat that are not already included in the program do not need to be included.



Weighing and Taking the Temperature of a Dough in the Fermentation Room

There seems to be little evidence indicating that minerals, other than iron and calcium, need be added to the diets of the American people. Iron is included as a mandatory ingredient in the enrichment program, while calcium is optional. However most white bread is made with milk solids, and Prouty and Cathcart (27) found that white bread as sold on the American market will average 0.08 per cent or about 0.4 gram of calcium per pound. Calcium is also added to bread by the general use of dough conditioners containing calcium salts.

#### January, 1943

Thus, the present enrichment program is developing along lines, in respect to vitamins and minerals, that will make enriched bread equivalent to whole wheat bread.

#### Production

Enriched flour and enriched bread can be produced by adding synthetic vitamins and iron to white flour and white bread. However, enriched flour can also be produced by special processes of milling that retain most of the vitamins and minerals of the original wheat. Such flours are darker in color and most of them do not meet the minimum standards for enrichment, so that when used for making bread some synthetic enriching materials must be added. However, it is possible for such flour to be made by milling alone that will produce bread meeting all the present requirements for enriched bread.

#### Loss of nutrients on baking

Thiamine is the only nutrient included in the enrichment program that shows loss in the processing of bread. Loss of riboflavin occurs when the slices of finished bread are exposed to light. However, the baking process does not affect it to any great extent (4). Neither niacin (19) nor iron (6) shows any appreciable losses, and there is no reason to suspect losses of calcium or vitamin D.

There is considerable loss of thiamine during baking and toasting of the bread. Findings on the loss of thiamine during the baking of bread range from approximately 5 to 30 per cent (23, 26, 29). A good average for commercial bread is believed to be 20 per cent (6, 26). Bakers must necessarily, then, add approximately 20 per cent more thiamine to their bread than required. There is no difference in the loss of thiamine in baking whether the thiamine comes from a natural or a synthetic source (29). The length of baking time seems to be the most important factor in the amount lost during baking; the greater the baking time, the greater the loss of thiamine (26). The temperature of baking also has some affect; the higher the temperature, the greater the loss.

On toasting bread there is a still further loss of thiamine, which varies from 0 to 25 per cent; the average for medium toast is approximately 17 per cent (8, 29). Thiamine, however, can be added to other products which would apparently not retain it so well as bread—for example, self-rising flour biscuits. Barackman (5) showed that the loss of thiamine during the baking of the biscuits is only 15 per cent, provided the pH of the baked product is 7.1 or lower.

#### **Progress of enriching program**

Even with all these difficulties the enriching program has made much progress; at present, with the full support of the milling and baking industries and the backing of the Government, it has been estimated by different sources that approximately 65 per cent of all white bread made in the United States and 50 per cent of all family flour sold are enriched. A drive to increase the enriched family flour figure to 80 per cent is in progress.

Two states (South Carolina and Louisiana) have enacted laws that require enrichment of white flour and white bread. Both laws are in line with the standards for enriched flour and enriched bread given in Tables I and II.

Some companies, including the writer's, have not been satisfied with making bread that just meets the minimum requirements for enriched bread; they have added greater quantities of nutrients to reach whole wheat bread levels with respect to thiamine, niacin, and iron. These same bakers in general have enriched all of their white pan bread. This indicates the cooperation the industry in general is giving the Government in the enriching program. Yet, some bakers even today do not realize the importance of the program.

The present enrichment program, with the support the Government is giving it, presents the greatest opportunity the baking industry has ever had. By means of it the industry as a whole can produce bread of such nutritive value that food faddists will have little left to complain about. It puts bread in the preferred class of foods; that is, bread long recognized as an energy food now becomes a protective food as well. In fact, enriched bread brings substantially more thiamine to the dinner plate of all classes of people than vegetables and fruits (unless eaten raw), even though the latter are naturally good sources of this vitamin. This was brought to



Modern Traveling-Plate Bread Oven

light particularly by studies on noon meals of industrial employees by Goodhart (20). The typical meal, as estimated from published data on the nutritive value of the raw foods, was 0.9 mg. thiamine, which is a satisfactory figure for a noon meal. However, actual analyses of the entire meal as served showed only 0.073 mg., a loss of 92 per cent. Had enriched bread been included, it would have contributed the major portion of thiamine. More data of the above nature will be forthcoming in the future, when the destructive force of food processing on thiamine is fully realized.

The Government could help the program greatly by promulgating final standards for enriched bread that are approximately equivalent to those given in Table III. Bakers exercising control over their products would welcome such a standard. It should be pointed out, however, that the dietary labeling requirement now in effect helps serve as a check on the nutrients added.

Whether the ruling of the Seventh Circuit Court of Appeals, that vitamin D can be added to farina (standards are included with those for flour, 14) as an optional ingredient without actually producing enriched farina, will have any affect on the present enriched flour and bread program cannot be predicted at present. Some people have voiced the opinions that this ruling will leave standards of identity, especially those on enriched products, without any basis. The writer believes that the present enrichment program will continue in one form or another even if the ruling is upheld by a higher court.

#### Use of enriched bread by the armed forces

It has been specified that all flour purchased for the United States Army, Navy, and Marine Corps must be enriched in conformity with the proposed standards set forth by the Food and Drug Administration. The Quartermaster Corps has announced that all commercial bread purchased for army use must be enriched. This should make every baker and miller, as well as the public, realize that the Government is behind the present enrichment program, that there is benefit to be had from it, and that the various agencies responsible for the program intend to follow through.

Outside the special rations, enriched flour and bread are the only products being bought by the armed forces that have vitamins and minerals added to them. Undoubtedly, experiments similar to those of Goodhart (20) are responsible for making the Armed Forces realize the need for enriched flour and bread.

#### **Canadian** program

The Canadian program is considerably different from that outlined in the United States, mainly due to the fact that in Canada the addition of synthetic vitamins is not allowed. In fact, flour to which pure thiamine was added would be considered adulterated. This view is based upon the work of Canadian nutritionists involving the use of purified diets. They take the attitude that more than one or two vitamins are necessary in any deficiency case, and that the addition of one or two vitamins can seldom do much good (2).

Since at present there is apparent difficulty in increasing the thiamine content of flours naturally (that is, by milling alone), Canada was forced to set her standards rather low. Thus, the Canadian standard for vitamin B white flour (Canada Approved) has the minimum of 1.2 mg. thiamine per pound, while vitamin B white bread (Canada Approved) must have a minimum of 0.66 mg. (Bread must also contain 4 per cent milk solids based on flour.) Indications are that the Canadian millers are having some difficulty in producing flour to meet these standards (2, 6); yet the only specification is in regard to thiamine. The resulting Canadian Approved breads are slightly darker than regular white bread, but from all indications they seem to have fairly good consumer acceptance. However, some complaints have been registered.

## Nutritive value of enriched bread

Little has been done so far to determine by actual feeding tests on the finished bread the nutritive value of enriched bread as it is being made in the United States. However, most white bread made in the United States is made with milk; and with the milk supplementing the flour in calcium and proteins, enriched white bread should be approximately equivalent to whole wheat bread in nutritive properties. This is borne out by feeding experiments carried on by Light and Frey (25). These two workers have shown that white bread made with 6 per cent dry skim milk and 2 per cent enriched yeast (many bakers are using 2 per cent enriched yeast) based on flour enables the rat to grow as well as on whole wheat bread.

The general addition of vitamins and minerals to the vast quantity of bread now being enriched, where this bread is made approximately equivalent to whole wheat bread in its nutritive properties, is of significance to the health of the nation as a whole.

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# Short-time pasteurization of milk

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• • Certain problems connected with short-time pasteurization of milk have not been brought to a solution. The principles employed successfully in the scientific advancement of heat sterilization of canned foods are interpreted here so as to facilitate the application to milk pasteurization of a treatment analogous to that applied to canned foods. This interpretation is made in terms familiar to those acquainted with process calculation methods for canned foods.

A manner of using this method to solve the problems associated with milk pasteurization is described, with emphasis on the explanation

**F**OR years after milk pasteurization became a commerical process, the idea was prevalent that pathogens in milk could not be destroyed at a temperature below 60° C. (140° F.); in other words, 60° C. was considered a critical temperature that had to be attained if the dangerous microorganisms in milk were to be destroyed. Many believed that pasteurization could be satisfactorily accomplished only between 60° and 62.8° C. (145° F.).

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Later the idea gained acceptance that there is no critical lethal temperature, that any temperature high enough to have an unfavorable effect upon the growth and stamina of the bacteria is lethal, and that the bacteria will be destroyed if they are subjected to that temperature long enough. A corollary is the idea that, because less time is required to destroy bacteria at high than at low temperatures, advantages might be gained by pasteurizing milk above 62.8° C. With the growth of this thought the principle of high-temperature short-time pasteurization began to gain support.

Because of certain advantages of high-short pasteurization of milk, the long-hold form of pasteurization, exemplified by the customary exposure of market milk for 30 minutes at 61.1° to 62.8° C. (142° to 145° F.), has been yielding ground slowly but steadily to short-time methods in recent years. For market milk the minimum exposure accepted in highshort pasteurization is 71.1° C. (160° F.) for 15 seconds. An exposure commonly used is 71.7° C. (161° F.) for 16 seconds.

The growing use of the short-time form of pasteurization brings the necessity of increased stress on accurate time and temperature control, because a slight error in either time or temperature may have a much more serious effect in a shorttime process than in a long-hold process. Difficulty in establishing dependable temperature and time control has been one of the primary retarding factors to increased use of shorttime milk pasteurization.

Even with perfect manipulation of the process, one disturbing condition has occasioned much discussion. The counts of thermoduric bacteria are relatively high in milk which, according to standard criteria, has been adequately pasteurized by short-hold methods. A purpose of this paper is to of the high thermoduric bacteria counts in milk which has been adequately pasteurized by short-time methods. The use of the process evaluation method in the scientific solution of pasteurization problems must be inaugurated by the accumulation of data that can be used in determining significant values in thermal death time relations for the pathogenic and thermoduric microorganisms associated with milk pasteurization.

The manner of correlating this information with time-temperature curves for milk in the pasteurization process to evaluate the lethality of the process is illustrated by examples.

supply a scientific explanation of this phenomenon and at the same time to present an approach to a scientific attack upon the general question of lethal value of milk pasteurizing processes. To accomplish this purpose we turn to the principles of thermal death time that are applied in mathematical methods of evaluating canned foods processes.

An interpretation of these principles is necessary before a new application can be made. This interpretation can be presented most satisfactorily with the use of terms that are commonly employed in process calculation methods for canned foods; and although this material may appear to be foreign to the subject, it is an essential part of this presentation.

#### Evaluation of canned foods processes

FUNDAMENTAL PRINCIPLE. There are products through which heat penetrates so slowly that, in containers of large size, the center does not reach the temperature of the retort during a process of practical length. After heat penetration tests showed this to be true, it became clear that canned food processes could not be standardized from the standpoint of sterilizing value solely on the basis of the length of time the center of the can is held at retort temperature. The entire period during which the center of the can is at temperatures which are lethal to bacteria would have to be considered.

BASIS OF PROCEDURE. The key to evaluating a process for sterilizing value is found in the heat penetration curve and the thermal death time curve (2, 3, 4, 6-9, 13). Such a curve shows that the spores of a microorganism are destroyed in 10 minutes at 115.5° C. (240° F.) or in 360 minutes at 100° C. (212° F.). In terms of lethal effect, it is thirty-six times more intense at 115.5° than at 100° C. In other words, the intensity of the lethal effect is inversely proportional to the length of time required to destroy the organism. For a can of corn at 121° C. (250° F.), for instance, the effective energy which is in the act of destroying this spoilage organism at the point of maximum lag (point of slowest heating) in the can is thirty-six times as great when the maximum lag point is at 115.5° as when it is at 100° C. To evaluate the process, we must apply a sterilizing, or lethal, value to each temperature through which the maximum lag point of the can passes and add these together in such a way as to give full value to the length of time the maximum lag point is held at each temperature. During the time the temperature at the maximum lag point of the can is rising and falling, the point is at a given temperature only an infinitesimal length of time. Thus, to add the lethal effects for all temperatures, calculus must be employed.



Figure 1. Interrelation between Heating, Cooling, and Thermal Death Time Curves in the Calculation of Lethality

CALCULATION OF STERILIZING VALUE. The object in processing canned foods is the attainment of sterility with respect to the most resistant microorganism present which would bring about spoilage. Therefore the problem of determining the time necessary to process a canned food consists of determining the time necessary to produce this sterility within the cans. A method of computing this time is described by Bigelow *et al.* (6). This is the foundation of the calculation method described by Ball (2, 3, 4) and further developed by Olson *et al.* (11, 16, 22, 23).

Each minute section of the heating and cooling curves for the maximum lag point of a can, corresponding to a temperature that has lethal effect on spoilage organisms, is said to have a lethal rate value. This value, for any section, is the reciprocal of the number of minutes required to destroy all spores of the organism at the temperature represented by the midpoint of the section, under the condition obtaining within the food, times the length of the time period



represented by the section of the curve. These values are plotted against time, taken from the abscissas of the respective section mid-points of the timetemperature heating and cooling curves.

GRAPHICAL TRIAL-AND-ERROR METHOD. The method described by Bigelow is primarily graphical; the mechanics are illustrated in Figures 1 and 2. Figure 1 shows the timetemperature curves of the center of a can during heating and cooling, and the thermal death time curve of an organism. The curves are plotted side by side so that the same scale of degrees applies to all. The abscissas represent time; x' is time as determined in a heat penetration test of the can of food, x'' is time as determined in a laboratory test of the resistance of the microorganisms to heat. For the thermal death time curve, x'' is a scale of the reciprocals of the normal abscissa scale, x'. The broken lines join values on the x scale of processing time to values on the x'' scale of reciprocals of heat resistance time, which are plotted against each other in Figure 2. In this new curve, values from the x scale of Figure 1 are represented as abscissas, and values from the x'' scale as ordinates.

The area beneath the lethality curve (Figure 2) is equal to unity if the process represented by the heating and cooling curves of Figure 1 is just sufficient to destroy all spores of the organism; and the time, s (Figure 1), is then the length of process in minutes.

This is strictly a trial-and-error method of determining the length of a process necessary to sterilize a can of food. If the area beneath the lethality curve is either greater or less than unity, the process of solution must be repeated in order to determine the required length of process.

MATHEMATICAL METHODS—In more recently developed methods (2, 3, 4), the trial-and-error feature of the determination of sterilizing value is eliminated. A determination is made by direct mathematical calculations based on established formulas. The formulas are developed through the integration of lethal rate values assigned to the successive points of the heating and cooling curves of a can. To show graphically how this development is accomplished, a strip is taken along the heating and cooling curves which has a constant width of unity, measured in the direction of ordinates.



Figure 3. Heating and Cooling Curves, Showing Strip Which Is Integrated

This strip is divided into elements having infinitesimal horizontal width, dx. The elements extend across the strip in the direction of ordinates; therefore each element is of unit length and its area is (y + 1/2) - (y - 1/2) dx, which equals dx(Figure 3). Even though these elements have the same size, they do not all have the same value. Like gaseous molecules, each may be said to have its own weight. Just as the chemical atomic weight of an element is indicated by the position of the element in the periodic table, the atomic weight (lethal rate value) of each of these elements is indicated by the position of the element with respect to the temperature scale.

Figure 3 shows a heating and a cooling curve, symbolically enclosed within a strip, the vertical distance across the strip is 1 at all points. An element of the strip having an infinitesimal area, dx, is also indicated. Either the heating or the cooling curve passes through the exact center of every element. Each element may be said to have a temperature value, taken from the temperature scale along the left-hand border of Figure 3 at the elevation of the center point of the element.
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The temperature value of the element is significant in that it enables one to determine the "weight" of the element. which is dependent not only upon the area, dx, but also upon the lethal rate value corresponding to the temperature of the element. As explained previously, the lethal rate value is the reciprocal of the destruction time of a microorganism at a given temperature. This value is readily obtained with the assistance of the thermal death time curve for the microorganism, which shows the destruction time for each temperature. If, to each element is assigned a weight, dependent upon the lethal rate value corresponding to the temperature value of the element, it is obvious that a summation of the weights of all elements on the heating and cooling curves of a can will give the sterilizing value of the process represented by those curves. The weight of any portion of the strip which encloses the heating curve is expressed as the product of the lethal rate value and the area of the portion of the strip being considered—for example,  $0.1 \times dx$ , for an element having an area dx when the lethal rate value is 0.1.

To assist in developing a concept of this summation operation, we may assume that the heating curve in Figure 3 is extended to reach retort temperature,  $240^{\circ}$  F., and held at that temperature for a period of time. Along the horizontal portion of the curve (at 240°) all elements of equal size have equal weight. If we base a process upon a thermal death time curve of a microorganism that is destroyed in 10 minutes at 240° F., the weight of each of these elements is 0.1 dx. The area of all the elements on a portion of the heating curve extending over a distance represented by one minute of time is unity, or 1. The weight, therefore, of such a section of the strip is  $0.1 \times 1 = 0.1$ . It is clear that the weight, or sterilizing value, of the portion of the process during which the maximum lag point of the can is at 240° F. is 0.1 times the length of that portion of the process expressed in minutes.

The summation of "weights" of area elements along portions of the curves which represent changing temperature is more complicated than the summation for constant-temperature portions of the curve. The complete summation can be accomplished only by calculus. Calculus requires the use of mathematical equations for those curves. It was found that satisfactory equations could be developed for the heating, cooling, and thermal death time curves, on the basis that the thermal death time curve, the portion of the heating curve in which we are interested, and all of the cooling curve except the first part can be represented as straight lines on semilogarithmic coordinate paper, and that the first part of the cooling curve can be represented as a hyperbola.

A heating curve for a can and a thermal death time curve plotted on semilog paper are shown on Figures 4 and 5, respectively. Symbols representing some of the numerical properties, which are used in the calculation of processes, are shown. The standard symbol for designating the slope value of a heating curve is  $f_{a}$ , expressed as minutes, and of a thermal death time curve, z, expressed as ° F. The thermal death time curve on Figure 5 is considered the ideal destruction curve for Cl. botulinum.

After the equations have been derived, the area of an elementary portion of the strip enclosing each curve is expressed in terms of the equation of that curve. Each of these expressions (one for the heating curve, one for the hyperbolic part

of the cooling curve, and one for the semilogarithmic part of the cooling curve) is multiplied algebraically by an expression representing lethal rate value derived from the equation of the thermal death time curve. The resultant expressions represent the weights of the area elements in the strips enclosing the respective curves.



Figure 4. Heat Penetration Curve (Retort Temperature Equals 250° F.)

These expressions are integrated between the point at which the heating curve reaches a point  $80^{\circ}$  F. below retort temperature and the point at which the cooling curve reaches the same temperature. The integration leads to an equation in which the total "weight", A, of the strip enclosing the heating and cooling curves is represented by the algebraic expression,  $f_hC/t$ , where  $f_h$  represents the slope of the heating and cooling curves, t is the number of minutes required to destroy the organism at the highest temperature attained by the maximum lag point of the can in the process, and C is an arbitrary constant. When A = 1, the equation represents the condition of sterility. The solutions of processing problems are based upon this equation, which is solved with the use of a table giving values of C corresponding to different values of various factors.



Figure 5. Thermal Death Time Curve on Semilogarithmic Coordinates

The development of specific solution methods from this formula was accomplished through a long and involved process. Notable improvements in the use of the formula, resulting in simplification of calculations, have been made by Olson et al. (11, 16, 23).

#### Heat resistance investigations

CLOSTRIDIUM BOTULINUM. Thermal death time, or heat resistance, tests are made on cultures of pure strains of microorganisms. The most important in the problem of sterilizing nonacid foods is *Cl. botulinum*, because this organism secretes an extremely potent toxin. Thus, the first essential of every sterilizing process is that it be adequate to destroy the spores in this organism in the food. Although the spores are seldom present in food prepared for canning, it must be assumed, because there is no quick way of detecting them, that the spores are always present.

All known difficulties of heat resistance tests are encountered in working with the botulinus problem, whereas not all of the difficulties are met in dealing with certain other species of bacteria. Therefore, we shall discuss heat resistance with particular reference to protection of canned foods against *Cl. botulinum*.

For two reasons laboratories have avoided working with *Cl. botulinum* as much as possible: There is a health hazard, and *Cl. botulinum* has more than the usual degree of inconstancy in heat resistance of spores from different cultures.

No method is known of predicting heat resistance of spores of a given culture of this organism. Therefore, if a culture is produced with the intention of using it in processing studies, the chance is great that the organism will have low resistance to heat, and that results will be misleading in the establishment of processes because it must be assumed that *Cl. botulinum* of maximum heat resistance, as found by Esty and Meyer (8), might be present in food that is canned.

Because of these difficulties, attempts have been made to find harmless organisms of constant characteristics which might give results in laboratory tests similar to those that would be obtained with *Cl. botulinum*, should the latter have constant heat resistance. No organism entirely satisfactory for this purpose has been found. The one most frequently used, which, on the basis of general morphological traits, has been thought to be more like *Cl. botulinum* than any other nontoxic organism, is a putrefactive anaerobe, designated by National Canners Association as No. 3679 (American Type Culture Collection: *Clostridium sporogenes* No. 7955). This organism, however, is now declared to be fundamentally different from *Cl. botulinum* (13, 27).

But why, after heat resistance of *Cl. botulinum* has been determined, is it necessary to continue laboratory tests with the organism? The reason is that the heat resistance of an organism varies not only between strains, but even within a given strain, according to the type of food in which the organism is heated as well as to the type in which it is cultured. The organisms must be studied in every different food in all of its variations, and the resistance not only at one temperature but at four or five different temperatures must be determined so that the thermal death time curve applying to each given set of conditions will be established.

A single culture of an organism may have many thermal death time curves which differ from one another not only in absolute value for a given temperature, but also in slope (commonly designated by z), according to the food in which the organism is studied. The problems that must be solved in order to establish thermal death time curves for *Cl. botulinum* are set forth clearly by Townsend, Esty, and Baselt (27), who show why a complete thermal death time curve must be built up for each individual food, from laboratory experiments with the *Cl. botulinum* organism itself.



(Above) Glass, Sealed, Thermal Death Time Tubes, 7 Mm. I. D., 1 Mm. Wall (9); (below) Cotton-Stoppered Tubes, 16 Mm. I. D., 1 Mm. Wall (1, 5) 111

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Apparatus for Determination of Spore Destruction Rates (30)

FOOD-PHOSPHATE FACTOR. A practice followed to express the differences in resistance of spores in different media is to find the resistance of a particular strain of the organism in the food product in question and in buffered phosphate medium at only one temperature. The ratio of the two numerical values in minutes has been known as the food-phosphate factor. On the assumption that this ratio is constant for all temperatures and thus that all curves for *Cl. botulinum* have the same slope, the food-phosphate factor has been used to establish a tentative thermal death time curve for the organism in the particular food product being studied.

Discovery of the invalidity of this assumption revealed the weakness of the food-phosphate factor method of procedure in establishing processes for canned foods. The reason that organism 3679 is not a true substitute for *Cl. botulinum* in heat resistance tests is based on a related principle—namely, that with a given food, the two organisms give thermal death time data that are truly applicable to *Cl. botulinum*, therefore, must be obtained in tests made with the *Cl. botulinum* organism itself.

EVOLUTION OF HEAT RESISTANCE METHODS. In twenty years there has been an interesting evolution in methods of determining heat resistance of bacteria; and as this evolution has progressed, uncertainty has grown as to just what thermal death time is. The uncertainty is directly traceable to the complexity of those comparatively simple living organisms, the bacteria. The question we must answer is, "When are bacteria destroyed?"

Present practice in determining heat resistance as applied to the evaluation of canned food processes includes methods which may be put into five general classes. Five different types of apparatus are employed variously in carrying out these methods. Two of these types of apparatus are used with all classes of methods; the other three have selective applications to the methods. Some of these methods and techniques are described in the literature (7, 9, 30).

There has been an evolution in thermal death time test

procedure, advanced by a growing realization of the extreme complexity of this problem. The trend appears to be away from the procedures that show absolute destruction points and toward those that reveal rates of destruction of bacteria in terms of numbers destroyed in set periods at constant temperature, without proceeding to absolute destruction. This trend is based upon the principle that large numbers of units are capable of providing more consistent data than small numbers of units. In most rate-of-destruction tests bacteria are counted, whereas in tests designed to give absolute destruction points, containers, as a rule, are the units counted. Investigators feel that the most logical method for determining the destruction point of bacteria lies in determining rates of destruction by the plating method of testing.

The results of tests to determine rate of destruction of spores are conveniently recorded by rate-of-destruction curves, which show a relation between time and numerical strength. The time is that of heating the bacteria at a given temperature, and the numerical strength is the number of viable organisms per unit quantity of material. The normal rate of destruction of bacteria in a pure suspension at a constant temperature is said to be that of a chemical reaction. Although the rate usually increases more than twofold (as does a monomolecular chemical reaction) for each 10° C. rise of temperature, it seems safe to consider the normal rate-of-destruction curve to be a straight line on semilog paper (28). For the present, therefore, we shall disregard the possibility of having "sagging" or "bulging" curves, for which Rahn (20, 21) assumed various explanations. By definition, a reaction that proceeds at a logarithmic rate never reaches an end point; this means here that, if we heat an infinite quantity of material containing an infinite number of bacteria, we never destroy every bacterium, or if we heat a finite guantity of material containing a finite number of bacteria, we never completely destroy the last bacterium. In the broadest sense, therefore, theoretically there is no thermal death timethat is, a heating period at the end of which all bacteria are dead.



(Above) Thermal Death Time Cans (2<sup>1</sup>/<sub>2</sub> Inches in Diameter, <sup>3</sup>/<sub>8</sub> Inch High), Open and Assembled Courtesy, American Can Company

(Below) Cans of Commercial Size Used in Experimental Packs, Open and Assembled; Sample Is 2<sup>11</sup>/<sub>16</sub> Inches in Diameter and 4 Inches High

Fortunately we do not have to deal with an infinite quantity of material, so there is destruction of bacteria from the standpoint of preservation of canned foods. Figure 6 shows a rate-of-destruction curve plotted on semilogarithmic coordinates. In Figure 7 the same curve is plotted on paper with linear spacing of lines. The latter is a convenient method of plotting when it is desired to extend the curve through many cycles, since any major division of the scale may be used to represent a logarithmic cycle. The vertical scale in this method of plotting represents, instead of the actual

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Figure 6. Rate-of-Destruction Curve on Semilogarithmic Coordinates (Zeta = 68)

number of surviving bacteria, the logarithm of that number. Since the vertical coordinates are logarithms, the curve is still a straight line. The vertical scale could be expressed in terms of the logarithm of the percentage of surviving microorganisms without altering the curve essentially. The symbol, Z, for the slope value of the rate of destruction curve was suggested by Baselt. Z is expressed as minutes.

#### Building thermal death time curves

PHANTOM THERMAL DEATH TIME CURVE. To establish any semilog curve, two items of information are essential a slope value and the absolute location of one point. In canned food processing, the point usually chosen is that representing 250° F. (121° C.); its value, in terms of minutes, is designated by F. This is regarded as a reference point for all thermal death time curves.

If each rate of destruction curve passed through the point representing 100 per cent survival in nil time, the slope value, z, of the thermal death time curve could be obtained from a series of rate-of-destruction curves for an organism simply by plotting the slope values, Z, of these curves against temperature. Sometimes, however, there is no apparent reduction in number of viable microorganisms for a period of time after heating of the bacteria begins. This period is taken into account in deducing the value of z by the equation:

$$x = \frac{T - T'}{\log \left(x'_{100} - Z' \log \frac{a}{100}\right) - \log \left(x_{100} - Z \log \frac{a}{100}\right)}$$
(1)

One rate-of-destruction curve is chosen as a reference curve, for which T' represents temperature,  $x'_{100}$  represents the time in minutes during which there is no reduction in the number of microorganisms, and Z is the slope. T,  $x_{1u0}$ , and Z have corresponding meanings for any rate-of-destruction curve of the series. a is the percentage of original number of organisms surviving at the point of destruction, arbitrarily chosen as that for which slope value z is to be established.

The rate-of-destruction curve for the lowest temperature should be chosen as the reference curve. The value of ais allowed to be arbitrary because the expression,  $x_{100} - Z$ log (a/100), gives the time,  $x_a$ , corresponding to a per cent survival. Where this time is of no interest, a may be assigned a small value such as  $1^{-s}$ , in which case Equation 1 becomes:

$$= \frac{T - T'}{\log (x'_{100} + 10Z') - \log (x_{100} + 10Z)}$$
(2)

When we determine a value of z by Equation 1 or 2, we have what may be regarded as a thermal death time curve with direction but not position—that is, position with respect to destruction time or end point. Lacking this latter essential, the curve cannot have specificity or definite value in so far as the thermal death time coordinate is concerned. Therefore we shall call it a "phantom" thermal death time curve.

Use of this mathematical procedure associates the idea of incompleteness with the operation, which is desirable since the operation does not establish the real thermal death time curve.

CHOICE OF DESTRUCTION POINT. To obtain the second essential item of information, which gives position to the thermal death time curve, we must first determine what degree of destruction is necessary; in other words, we must establish a criterion for designating the point at which the ability of the bacteria to decompose the food is no longer indicated.

We may ask ourselves: "Should the required degree of destruction be indicated by two remaining viable organisms per unit of material, one organism per unit, one organism per two units, one organism per ten units, or should it be 0.01 per cent of the number present before heating, as some investigators have suggested?" The answer to this question will be unique for each organism under every different set of conditions. It will depend upon three factors—namely, the nature of the microorganism, the nature of the food under consideration, and the number of organisms originally present in the food. To obtain the correct answer through laboratory tests, clearly one must give careful consideration to three additional factors—namely, the temperature of culturing, the culture medium employed, and the number of organisms originally present in the test suspension.

The use of a container, whether it be tube or can, as the unit to be counted in establishing results has been criticized by some investigators, because the last spores to remain viable in a run do not germinate readily under certain conditions of subculturing or of direct culturing. Such criticism indicates that the culturing technique is an important factor in viability tests, and that this technique must be chosen according to what the object of the test is.

It appears that the difficulty in producing growth in the last few organisms to survive a heat treatment may be caused by the fact that the severe heat treatment has deprived these organisms of a portion of their vitality. The condition may be purely a phenomenon of delayed germination.

The difference between the effect of this phenomenon upon the results of subculturing in peptone-dextrose broth, for example, and the effect upon the results of plating in tryptonedextrose broth and agar is no doubt one of degree only. It may be unreasonable to expect that all bacteria—still vital, although injured by heat—will produce colonies on agar plates. Therefore, under any method of testing there may always be some vital spores remaining which cannot germinate within the time usually allowed in laboratory determinations.

MATING OF BACTERIA. If one wishes to give free rein to his imagination, he may conclude that the apparent lack of 31

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vitality in tests by laboratory culturing technique, of the last few remaining organisms which our curves indicate are still vital, is accounted for by the existence of a sex characteristic in bacteria, and that with the organism so sparsely distributed, opportunity for mating is not afforded. Of course, there are many known facts regarding the propagation of bacteria



Figure 7. Rate-of-Destruction Curve on Linear Coordinates

which discredit such a theory. Efforts of Sherman and Wing (24) to reveal sex in bacteria were futile; nevertheless the fact that the possibility of mating is not to be discarded too lightly is impressed on those who read Jennings' report (12) of his pryings into the private lives of certain single-cell organisms, the ciliate infusorians. Jennings considers the plausibility of the mating of these organisms, and his discussion of under-par individuals indicates a possible explanation of the apparent low virility of spores that have been severely heated. Some may be able to germinate after a long period; others may never be able to germinate even though presumably they are still vital. On this hypothesis an adequate sterilizing process may be defined as one that will carry bacterial flora into the stage in which any vital bacteria that remain will not be able to germinate.

TESTS TO DETERMINE END POINT. Viewing the situation in the light of these circumstances, one must consider carefully the question of what is the best practicable test to reveal the destruction points of spores. Since any destruction point based on the results of either laboratory or practical test must be, at best, an arbitrary point, the choice of a method to determine such a point should depend upon which arbitrary point appears to bear the most consistent relationship to the conditions existing in actual commercial processes. Logically, it is necessary to assume that a similar condition of delayed germination may exist in cans packed commercially to that existing in tubes and plates in the laboratory. Furthermore, if we are to believe what our curves tell us, that some small percentage of the bacteria will always remain vital, perhaps we should assume that the last few vital organisms will never germinate.

Several avenues of attack on this problem are open. They

will not be discussed except for the statement that a logical laboratory test to establish a basis for choice of a destruction point is to culture portions of material containing very small numbers of vital spores, taken during the latter part of a heat resistance run, in food identical to that for which processes are being studied. The results of such culture tests give a good indication of what degree of destruction might reasonably be considered the destruction point, or the disabling point, of the spores in that particular food.

Even after this has been done, the thermal death time will still be shown only conditionally by rate-of-destruction curves. We shall have found the end point, but the beginning point will then have to be considered. What number of spores per unit of food material did we have The rate-of-destruction curve shows clearly that originally? the smaller the original number of bacteria, the shorter the time required to reach the end point unless the end point is expressed as a percentage of the original number. For instance, Figures 6 and 7 show that there were about 21,000 spores in each unit of material at the beginning of the test represented by the rate of destruction curve. The time scale to the left of the zero point in Figure 7 indicates the additional time that would be required to reach any given degree of destruction if the number of spores originally present were greater than 21,000 per unit of material. For example, if there had been 1.000.000 spores per unit of material, almost 125 minutes longer would have been required to destroy them than was necessary with 21,000 spores per unit of material. This effect of numbers upon destruction of bacteria constitutes additional objective knowledge which cannot be explained by known facts pertaining to the nature of bacteria. Why should animate cells, in their reaction to heat, exhibit properties similar to those of inanimate molecules in a chemical reaction? The answer to this question must lie in the fact that the reactions that destroy bacteria are chemical.

#### **Experience** in processing

The implication carried by the conclusion, reached on the basis of theoretical analysis, that foods originally infected with microorganisms can never be completely freed from them by sterilizing processes would be disturbing were it not for practical experience. For the last fifteen years, during which processes have been established with the use of thermal death time results that were based on the assumption of complete destruction of microorganisms, experience has validated that assumption from a practical viewpoint. At any rate, it has shown that if vital organisms do remain in the food after processing, they are in such a state that they can do no harm.

During this period at least a hundred billion cans of food susceptible to spoilage by *Cl. botulinum* have been placed on the market. Surely there were spores of *Cl. botulinum* in a portion of that food when it was canned. Reasoning from the indications of rate-of-destruction curves, we should conclude that some of these spores in a hundred billion cans survived the sterilization process. Perhaps they did; nevertheless, they produced no evidence of their survival.

#### Taken-for-granted safety

Circumstances of this nature apply to food of many types. Hypothetical speculation leads us to a realization of the existence of many possible bacterial hazards in our everyday foods. Experience in the common use of these foods without ill effects has inured us to this possibility; apparently the hazards do not actually exist even though we cannot explain fully why they do not. For example, since *Cl. botulinum* is a soil organism widely distributed in the United States, soil particles on many root and tuber vegetables prepared in the home, such as carrots, turnips, and potatoes, must be in-



Figure 8. Thermal Death Time Curves of Pathogens, and Phantom Curves Used in Calculations

fected with spores of this organism. When these foods are prepared in certain ways, anaerobic conditions will exist and presumably provide satisfactory environment for normal growth of the spores while the prepared foods are held before use. Still, records fail to report a single case of botulism from such foods.

Consider even pasteurized milk. Rate-of-destruction principles would convince us that, even in perfectly pasteurized milk, if the amount of milk is great, some vital nonsporeforming pathogens will remain. Experience teaches us that, in effect, this is not true.

These are samples of "taken-for-granted" safety in foods, safety which our most advanced theoretical knowledge tries to convince us does not exist, but which experience, supplemented by actual scientific tests, shows does exist. We must be cautious, however, lest we become so accustomed to taking for granted the safety of processed foods that we forget to apply adequate safeguards when changes in processing procedure are made.

The ordinary boiled and baked hams of commerce have been accepted without question for years, and have never been responsible for a case of gastrointestinal irritation from bacterial cause except when the ham was grossly mishandled. Yet during 1940 seventeen cases of food poisoning were traced to organisms of the staphylococcus group occurring in tendered hams. This is a small number of cases compared to the number of hams consumed; but it is enough to indicate that tendered ham may be more susceptible to growth of this organism than were the types of hams to which we were formerly Vol. 35, No. 1

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accustomed, in which there was an element of safety apparently not present in the new. Moulton (14) attributes the contamination of the hams with the organism to carelessness on the part of the packer, retailer, or consumer. Contamination may have been no greater than in the old style product. Perhaps the organisms simply had a better chance to develop than formerly, due to a different chemical environment.

In 1938 a small amount of trouble was experienced because of the growth of two highly heat-resistant strains of mold in No. 10 cans of blueberries. For destruction of the spores, Williams et al. (29) found that a heat treatment of approximately 10 minutes at 200° F. was necessary. It was evident that the spores were not destroyed by the sterilizing process ordinarily used for the product. The question immediately arose as to why these organisms had not caused trouble before. The answer seems to lie in the factor of oxygen in the can. Both strains are capable of growing in vacuum of 26 inches. This indicates that the amount of oxygen required for their growth is extremely small. It appears that even this small amount of oxygen was not available in the processed cans when so-called plain cans (no enamel linings) were used. When a change was made to enamel-lined cans, however, the absorption of oxygen within the cans was retarded because the covering of the catalytic metal was sufficient to permit growth of the mold in the can for a limited period. This explanation is only tentative, and the matter is receiving further study.

The warning of science to industry from the ham and blueberry experiences is that the effects of taken-for-granted factors should be recognized as early as possible, even though

these effects are not understood, and that changes of procedure or of associated conditions which might have a significant influence on taken-for-granted factors are to be avoided unless they are accompanied by measures to counteract any reduction in safety factors that the changes might produce.

REFINEMENT OF TECHNIQUE. This searching for better methods of finding the destruction points of bacteria is merely a part of a process of refinement of technique for the purpose of placing our attack on the processing problem onto a broader plane, so as to bring into consideration more and more of the influencing factors and to put our findings onto a more definite basis. In other words, we are taking steps to answer the question "Why?" as applied to matters that have had to be taken for granted.

The logical expectation from the application of the rateof-destruction principle to thermal death time determination is that, when we succeed in making it work, we shall have knowledge of the control of bacteria that will permit us to reduce processes with safety from those now regarded as necessary. There must be many combinations of conditions not yet understood, under which organisms will not grow.

#### Milk pasteurization processes

Most of the problems associated with milk pasteurization can be solved by application of the principles just explained, notwithstanding the uncertainty that still exists in respect to some of them. Rate-of-destruction curves for the 13

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non-spore-forming pathogens yield phantom thermal death time curves which, when combined with time-temperature heating, holding, and cooling curves for milk in the pasteurization processes, enable direct comparisons of lethal values of different pasteurization processes to be made with respect to individual organisms, both pathogenic and thermoduric.

Fortunately, experience often comes to our rescue when we seem to be stopped on the theoretical path. In the present case experience in pasteurization provides the information required for establishing real thermal death time curves after phantom curves have been obtained from results of rate-ofdestruction tests.

If one desires only to calculate a process that is equivalent in lethal value with respect to a specified microorganism to a given process which is known to be adequate to destroy that organism, the slope is all that needs to be known about the thermal death time curve. In other words, the phantom thermal death time curve, together with one process that is satisfactory in practice, is sufficent to establish the real thermal death time curve for the microorganism and, from this. to establish other processes. Thus, a given process serves the same purpose, in establishing the position of the thermal death time curve, as an end point of destruction would serve if determined by thermal death time tests in the laboratory. Standard calculation procedure provides a simple way of finding the F value of a curve when the heat penetration curve and the phantom thermal death time curve are known.

There are statements in the literature (25, 26) to the effect that pathogens are destroyed to an equal extent by the highshort process of 16 seconds at 71.7° C. (161° F.) as by the long-hold process of 30 minutes at 61.7° C. (143° F.), but that this is not true with respect to thermoduric bacteria. This means that slope values, z, of thermal death time curves for pathogens are lower than those for thermodurics. The simplest explanation of the significance of variations in z is that the lowest z value implies the highest relative sterilizing value for a high temperature as compared to that of a low temperature. For example, if two microorganisms have thermal death time of 30 minutes at 61.7° C. (143° F.), but the thermal death time curve for one has a slope of 18° F. (10° C.) whereas that of the other has a slope of 9° F. (5° C.), the sterilizing value of 1 minute at 71.7° C. (161° F.) will be ten times as great with respect to the latter organism as to the former.

If we examine pasteurization specifications of 16 seconds at 71.7° C. and 30 minutes at 61.7° C. in the light of the thermal death time curve principle, we find that any organism for which these two processes hold equal destruction value has a thermal death time slope value of only  $8.7^{\circ}$  F. ( $4.8^{\circ}$  C.). This is indicated by curve S on Figure 8, which passes through points P and Q representing, respectively, the two specified processes.

This statement assumes that no time is required to heat the milk to the set temperature of either  $71.7^{\circ}$  or  $61.7^{\circ}$  C. or to cool it at the end of the process; that is, the milk in every case is brought to the pasteurizing temperature instantaneously and is cooled instantaneously. Such an assumption is contrary to fact. In all cases time is required to heat the milk to the designated holding temperature for pasteurization. To take this into account in a study of pasteurization by the method used for canned food sterilization, one must indicate the temperature of the milk during its rise to the holding point by a curve which will occupy a place in this problem analogous to that of the heat penetration curve in problems on canned food processing. Similarly, one must represent the rate of cooling by a time-temperature curve.



Courtesy, Cherry-Burrell Corporation Milk Pasteurizer of Short-Hold Type, Plate Construction

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The ascribing of comparatively low z values to thermal death time curves for microorganisms of low heat resistance is consistent with practice in canning process studies. In process calculations to cover destruction of nonspore formers in tomatoes, for example, a z value of approximately 14° F. (7.8° C.) has been considered correct, as compared with 18° F. (10° C.) which is most commonly used for spore formers in nonacid products. Williams *et al.* (29) found thermal death time curves for the faculative anaerobic mold in blueberry a process of the faculative anaerobic mold in blueberry as the faculative anaerobic mold in blueberry as the faculative state.

juice, previously described, to have a slope value of about  $10.5^{\circ}$  F. (5.8° C.) Our studies with nonacid foods have never carried us into the use of z values in the extremely low region that seems to be called for in high-short pasteurization work.

Table I. Lethality Constants of Heating and Cooling

<b>Portions of Milk Pasteurization Process</b>									
₂ Va ° C.	lue ° F.	Constant A R or A.	Constant B	Constant C	Constant D				
3.34	6	243	116	32.9	1.19				
3.89	7	288	123	38.3	1.39				
4.45	8	332	129	42.8	1.58				
5.00	9	376	134	46.8	1.78				
5.55	10	421	139	50.3	1.97				
6.11	11	466	144	- 53.6	2.172.362.562.762.95				
6.67	12	510	148	56.6					
7.22	13	554	152	59.3					
7.78	14	599	155	61.9					
8.33	15	644	158	64.3					
8.89	16	688	161	66.6	3.15				
9.44	17	732	163	67.8	3.34				
10.0	18	777	166	70.6	3.54				
10.5	19	821	168	72.4	3.73				
11.1	20	866	171	74.2	3.93				
11.7 12.2 12.8	21 22 23	910 955 1000	173 175 177	75,8 77,4 78,9	4.13 4.32 4.52 4.71				

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By the use of arbitrary constants, the lethal value of the temperature rising and declining periods of the pasteurization process can be readily calculated, based on assumed rates of rise and decline of temperature. Table I contains lethality constants A, B, C, and D, respectively, for four different rates of rise and decline of temperature. Simple calculations will convert the constants into percentage values referred to the amount of lethal heat set as the requirement of the process. For example, if 30 minutes at  $61.7^{\circ}$  C. is regarded as the measure of sterilization required for a given microorganism, conversion of the constants in Table I will give the amount of lethal heat that is effective during the periods of temperature rise or decline, expressed as a percentage of the amount required for the process.

Assuming that the phantom thermal death time curve for the microorganism is known, a thermal death time curve having the slope value of the phantom curve and passing through the point representing 30 minutes at  $61.7^{\circ}$  C. will show for all temperatures the times required to give sterilizing effect equivalent to heating for 30 minutes at  $61.7^{\circ}$  C. when both the rise to and decline from holding temperature are instantaneous. The percentage values yielded by the constants of Table I apply to the period of rise to or decline from the holding temperature, regardless of what that temperature may be.

A factors in Table I apply to either a uniform rate of rise from initial temperature IT to holding temperature HT, or of decline from holding temperature HT to final temperature FT—that is, a change through a constant number of degrees during each successive unit of time. For example, curve  $A_{RT}$  (Figure 9) represents heating during 7 minutes, curve  $A_{\sigma}$ , cooling during 7 minutes.

Since heating is by indirect means in milk pasteurization, the rates of heating and cooling ordinarily are not expressible as simple linear functions. They seem more nearly to resemble semilogarithmic functions. Factors B, C, and Dapply to semilogarithmic rates in various modifications.

B factors of Table I apply to a heating rate represented by a straight line on semilog paper (Figure 9). Since such a curve would go to infinity unless it were defined, a termination at some point below holding temperature must be specified in order to establish a slope value for a rise of temperature within a stated time. B factors were determined on the basis of terminating the rise of temperature 0.056° C. (0.1° F.)below the holding temperature, HT.

C factors are analogous to B except that the curve is made to terminate 0.56° C.  $(1.0^{\circ} \text{ F.})$  below holding temperature, HT. They apply to the heating period only (Figure 9).

D factors apply to a cooling rate represented by a straight line on semilog paper (Figure 9) the terminating point of which is supplied optionally for each calculation. The terminating point is expressed as the number of degrees above the temperature of the cooling medium, CW, and is represented by  $g_e$  for Fahrenheit and 0.56  $g_e$  for centigrade.

A lag factor, commonly represented by j, is essential in semilogarithmic heating and cooling curves. Factors B, C, and D are based upon j = 1.0, which seems reasonable for convection heating of a liquid product in mechanical agitation. Knowledge of this value is not essential to carrying out these calculations.

The calculation of the percentage values for lethal effect during the periods of rising and declining temperature are made by Equations 3 to 7:

A for heating period: 
$$p_{RA} = \frac{A_R t_{RA}}{U(HT - IT)}$$
 (3)

A for cooling period: 
$$p_{eA} = \frac{A_{e}t_{eA}}{U(HT - FT)}$$
 (4)

B for heating period: 
$$p_B = \frac{Bt_{RB}}{U[\log{(HT - IT)} + 1]}$$
 (5)

C for heating period: 
$$p_C = \frac{Ct_{RC}}{U \log (HT - IT)}$$
 (6)

$$D \text{ for cooling period: } p_D = \frac{Dt_{cD}}{U[\log\left(HT - CW\right) - \log g_c]}$$
(7)

where  $p_{RA}$ ,  $p_{cA}$ ,  $p_B$ ,  $p_C$ ,  $p_D = \%$  of required lethal heat  $A_R$ ,  $A_c$ , B, C, D = arbitrary constants from Table 1 HT = holding temp. of pasteurization process IT = initial temp. of milk FT = final temp. of milk after cooling CW = temp. of cooling medium  $t_{RA}$ ,  $t_{RB}$ ,  $t_{RC}$  = time consumed in rise of temp. of milk, min.  $t_{cA}$ ,  $t_{cD}$  = time consumed in decline of temp. of milk, min. U = time necessary to destroy microorganism at holding temp., min.  $g_c$  = difference between FT and CW, degrees

The time during which the milk must be held at holding temperature HT in order to give adequate pasteurization when time is consumed in the rise and decline of temperature of the milk for different combinations of rates of heating and cooling is given in Equations 8 to 13:

Rate of heating 
$$A$$
  
Rate of cooling  $A$   $t_{HAA} = U - \frac{0.01 A_R t_{RA}}{HT - IT} - \frac{0.01 A_c t_{eA}}{HT - FT}$  (8)

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Rate of heating 
$$A \downarrow t_{HAD} = U - \frac{0.01 A_R t_{RA}}{HT - IT} - \frac{0.01 D t_{eD}}{\log(HT - CW) - \log g_e}$$
 (9)

Rate of heating 
$$B$$
  
Rate of cooling  $A$   $t_{HBA} = U - \frac{0.01 B t_{RB}}{\log(HT - IT) + 1} - \frac{0.01 A_c t_{cA}}{HT - FT}$  (10)

Rate of heating B  
Rate of cooling D 
$$t_{HBD} = U - \frac{0.01 B t_{RB}}{\log (HT - IT) + 1} - \frac{0.01 D t_{eD}}{\log (HT - CW) - \log g_e}$$
 (11)

Rate of heating 
$$C$$
  
Rate of cooling  $A$   $t_{HCA} = U - \frac{0.01 C t_{RC}}{\log (HT - IT)} - \frac{0.01 A_c t_{cA}}{HT - FT}$ 

Rate of heating C and  $t_{HCD} = U - \frac{0.01 \ Ct_{RC}}{\log (HT - IT)} - \frac{0.01 \ Dt_{cD}}{\log (HT - CW) - \log g_c}$  (13)

# where $t_{HAA}$ , $t_{HAD}$ , $t_{HBA}$ , $t_{HBD}$ , $t_{HCA}$ , $t_{HCD}$ = time milk is held at holding temperature, HT, under different combinations of rates of heating and cooling, min.

The second and third terms in the right-hand member of each equation express lethal values of heating and cooling periods, respectively, as minutes of heating at the holding temperature, HT. For example, if in Equation 13 0.1  $Ct_{\pi c/}$ log (HT-IT) equals 2.5, this fact would signify that the coming-up period is equivalent in sterilizing value to 2.5 minutes at holding temperature HT.

DATA IN DESTRUCTION OF BACTERIA. Most of the data in the literature are of such form as to be of no value in establishing thermal death time curves. They usually indicate only isolated points, and controlling conditions, such as concentration of organisms and rate of rise of temperature, are not specified. The following quotation from Hammer (10, page 136) is typical of the presentation of these data:

Rosenau found that *E. typhosa* was killed in milk heated to 60° C. (140° F.) and maintained at this temperature for 2 minutes; the great majority of the organisms was killed by the time the milk reached 59° C. (138.2° F.), and only a few survived at 60° C. *C. diphtheriae* often failed to grow after the milk reached 55° C. (131° F.), although occasionally it survived until the milk reached 60° C. The resistance of *V. comma* was similar to that of *C. diphtheriae*; it was usually destroyed when the milk reached 55° C. but once it lived until 60° C. was reached.

Figure 8 shows five thermal death time curves plotted from the only data found in the literature on pathogenic organisms in milk for which a destruction point at each of three or more temperatures in a single series of determinations was given. The curves are described in Table II.

These data were taken from Hammer (10). The rate of heating or of cooling was not stated for any of the destruction points given, nor were the intervals of time between readings for four of the five tests. The concentration of microorganisms was stated for Br. suis only. When time was stated somewhat indefinitely—for example, "less than 7 minutes"—the exact time of destruction had to be estimated.

An important feature of these data lies in the fact that some bacteria probably were destroyed while the temperature was rising, but since the rate of rise is not given, the absolute lethal value of the nominal process is not revealed.

(12)

The number of minutes indicated by the thermal death time curve of each organism as the resistance at 60° C. (140° F.) is given in Table II under the heading  $PU_{140}$ , a symbol invented by Benjamin for "pasteurization unit". Designating a point on a curve, this value serves the same purpose for reference and placement of the curve in the pasteurization temperature range as F does for curves in canned foods process range.

Other data in the literature on the nonspore-forming bacteria include information on resistance of five types of such bacteria in phosphate solution and broth. Beamer and Tanner (5) and Baker and McClung (1) published rate of destruction curves for such organisms. The former included *Eberthella typhosa*, Salmonella paratyphi, Salmonella aertrycke, Salmonella enteritidis, and Staphylococcus aureus in broth of pH 7.05; the latter studied *Escherichia coli* in phosphate solution of pH 7.00.

Slope values of phantom thermal death time curves from these data are given in Table III. Those for *Eberthella typhosa* and *Salmonella aertrycke* and the first of those for *Escherichia coli* are rather clearly defined by the values taken from the data while those for the other organisms are indefinite because the three  $x_a$  values taken from the data for each type of bacterium do not indicate a straight line.

CALCULATION OF LETHALITY OF PASTEURIZATION PROC-ESSES. Neither Table II nor III contains data on bacteria of

able II.	Thermal D	Death Time	e Curve	Data for	Pathogens	in Milk	(10)
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Curve No.	Microorganism	No. per Ml.	Medium in Which Heated	No. of Points Given	<u>z V</u> ◦ C.	alue ° F.	PU140	Reference
1 2 3	E. typhosa M. tuberculosis M. tuberculosis	Not given Not given Not given	Cream Cream Milk	3 4 8	8.5 7.0 6.9	$15.3 \\ 12.6 \\ 12.4$	4.5 9.2 14.0	(15) (15) (17)
4	(Br. abortus )	Not given	Milk	3	8.0	14.4	8.6	(18)
5	(Br. melitenis) Br. suis	500,000,000	Milk	3	5.1	9.2	23.0	(19)

Table III. Data on Nonspore-Forming Bacteria

						200.00000001					
Bacterium	Medium in Which Heated	pН	51.7° C. (125° F.)	54.4° C. (130° F.)	55° C. (131° F.)	57.2° C. (135° F.)	60° C. (140° F.)	62.8° C. (145° F.)	65° C. (149° F.)	• C.	• F.
Eberthella typhosa (6) Salmonella parathyphi (6) Salmonella antrycke (6) Salmonella enteritidia (6) Stanbucceus auras (6)	Broth Broth Broth Broth Broth	7.05 7.05 7.05 7.05 7.05 7.05			40 32 40 46 300	···· ··· ···	8.6 10 13 13 33		1.6 1.7 4.3 6.4 10	7.3 8.6 10.5 10.9 6.1	13.1 15.5 18.9 19.6 11.0
Escherichia coli (1) Escherichia coli (1)	Phosphate Phosphate	7.00 7.00		350 13		158 6	52	23	::	6.6 5.1	11.9 9.2

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Figure 9. Hypothetical Heating and Cooling Curves for Milk in Pasteurization Process

thermoduric type, therefore it is impossible to state definitely that thermal death time curves for thermodurics in milk have greater slope values than those for pathogens in milk. Most spore formers in nonacid media have thermal death time curves with slope values in the general vicinity of 10° C. (18° F.) and some have higher values. Assuming that a typical thermoduric microorganism in milk has the same z value as that shown in Table III for Salmonella aertrycke-namely, 10.5° C. (18.9° F.)-calculations show how processes at 71.7° C. (161° F.) that are equivalent with respect to this organism to a given process at 61.7° C. (143° F.) compare with processes at the former temperature that are equivalent with respect to Br. suis to the same given process at 61.7° C.

Phantom thermal death time curves for these two organisms, passing through point P representing 30 minutes at 61.7° C., are indicated by lines X and Y on Figure 8. The intersections of these lines with the temperature coordinate representing 71.7° C. at points T and  $\hat{V}$  give the holding times at 71.7° C. which are equivalent, respectively, to 30 minutes at 61.7° C. with instantaneous heating and cooling in all cases. These times are 19.2 seconds for Br. suis and 3 minutes 20.4 seconds for S. aertrycke.

To illustrate the effects of various rates of heating and cooling, in conjunction with variation in z value, upon the lethality values of the processes, 140 calculations were made: the results are shown in Tables IV and V. Heating and cooling times of 0, 7, and 15 minutes were assumed with all combinations of heating rates  $A_{R}$ , B, and C with cooling rates  $A_{\epsilon}$  and D (Table I).

The heating time  $t_H$  required to give, in combination with heating and cooling periods, lethal effects equivalent to those of processes with instantaneous heating and cooling as indicated by the phantom thermal death time curves were calculated by Equations 8 to 13. To give analogous comparisons in other terms, the per cent p of adequate lethal heat supplied by each process when  $t_{H} = U$  was calculated, thus indicating clearly how much lethal heat is accounted for by the coming-up and cooling periods. When  $t_H = U$ , the holding period, t<sub>H</sub>, accounts for lethal heat equal to 100 per cent of that required to pasteurize. The latter computations were made by evaluating the righthand members of Equations 8 to 13 after changing the signs between terms from minus to plus, dividing the result by the value of U, and multiplying by 100.

#### **Discussion of results**

The outstanding fact revealed by these calculations is that when U has a value of  $3^{1}/_{3}$  minutes or less, the heat applied during coming-up and cooling periods may be a major portion of that required for pasteurization. extreme condition shown is in the processes for Br. suis at 71.7° C. (161° F.). At this temperature 19.2 seconds are sufficient to destroy Br. suis, and if 15 minutes were used to bring up the temperature at heating rate B, the heating period alone would supply almost twenty-one times as much lethal heat as is needed to destroy the organism.

In a process in which p = 200, the lethal heat of the comingup and cooling periods combined is just sufficient to destroy the microorganism; therefore the required holding time is nil. When p > 200,  $t_H < 0$ , as indicated in Table V for numerous processes at 71.7° C. The latter condition signifies that pasteurization is accomplished without heating the milk all the way to HT.

The maximum amount of lethal heat contributed by a coming-up time of 15 minutes when U = 30 minutes is 28 per cent (process 16, Table IV) and the maximum for comingup and cooling periods combined (each 15 minutes long) is 34 per cent (process 17 for S. aertrycke, Table V)

The cooling period has little value compared to that of the coming-up period except when both rise and decline of temperature occur at rate A, in which case the values of the two periods are identical.

The maximum length of the coming-up and cooling periods-namely, 15 minutes-chosen for these calculations is great compared to the length commonly used in practice. Nevertheless, inspection of the p values for Br. suis (Table V) makes it clear that, even though the period were only 1 to 5 minutes in length, its value would be appreciable compared to that of the holding period.

In the interpretation of these results, it is essential to keep in mind that, although they are based upon phantom thermal death time curves, they give accurate comparisons between different processes at the same or at different processing temperatures. Table V indicates sterilizing values for proc-esses at 71.7° C. (161° F.) which are strictly comparable to the values given in Table IV for processes at 61.7° C. (143° F.) for Br. suis and S. aertrycke as they are represented by available heat resistance data. If the processes at 71.7° C. are longer than necessary, it is because the process of 30 minutes at 61.7° C. is correspondingly long.

The fact that the coming-up periods of short-time pasteurization processes in practice customarily have not been taken into account in the experimental evaluation of

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#### Table IV. Lethality Values of Processes at 143° F. (61.7° C.)

 $UT = 40^\circ$  F. or 4.4° C.;  $\sigma_s = 1^\circ$  F. or 0.56° C.; U = 30; tH for each process when just

		Rate of Temp.		Rate of Temp.	FT,	CW,	Br. z = 9	suis .2° F.	S. acrz = 18	trycke .9° F.
No.	t <sub>R</sub>	Rise	t a	Decline	° F.	° F.	tH	р	tH	p
1 2 3 4 5	0		0 15 7 15 7	A A D D	40 40 40 41 41	40 40	$\begin{array}{r} 30.00 \\ 29.44 \\ 29.74 \\ 29.86 \\ 29.94 \end{array}$	100.0 101.9 101.0 100.5 100.2	30.00 28.81 29.44 29.73 29.87	100.0 104 0 101 9 101.0 100.5
7 8 0 10	15	A	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	29.44 28.88 29.18 29.30 29.38	101.9 103.8 102.8 102.3 102.1	28.81 27.62 28.25 28.55 28.68	104.0 108.0 105.9 104.8 104.4
11 12 13 14 15	7	A	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	$\begin{array}{r} 29.74 \\ 29.18 \\ 29.48 \\ 29.60 \\ 29.68 \end{array}$	101.0 102.8 101.8 101.3 101.1	29.44 28.25 28.89 29.18 29.37	101.9 105.9 103.7 102.9 102.3
16 17 18 19 20	15	В	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	23.27 22.71 23.01 23.13 23.21	122.4 124.2 123.3 123.0 122.6	21.63 20.44 21.07 21.36 21.50	128.0 134.0 129.8 129.0 128.4
21 22 23 24 25	7	В	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	$\begin{array}{r} 26.87\\ 26.31\\ 26.61\\ 26.73\\ 26.86\end{array}$	110.4 112.3 111.2 111.0 110.4	26.06 24.87 25.50 25.79 25.93	113.2 117.1 115.0 114.0 113.7
26 27 28 29 30	15	С	0 15 7 15 7	A A D D	40 40 40 41 41	 40 40	$\begin{array}{r} 26.48\\ 25.92\\ 26.22\\ 26.34\\ 26.42 \end{array}$	111.7 113.7 112.7 112.3 112.0	24.61 23.42 24.05 24.34 24.48	118.0 122.0 119.9 119.0 118.3
31 32 33 34 35	7	С	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	28.40 27.84 28.14 28.26 28.39	105.3 107.2 106.2 105.8 105.3	27 49 26.30 26.93 27 22 27.36	108.3 112 3 110 3 109.3 108.8

which is that the rate of reaction doubles for each increase of temperature of  $10^{\circ}$  C. or  $18^{\circ}$  F.

The time-temperature curve of inactivation will have a slope value that is unique for the conditions under which the inactivation is accomplished. On the simple monomolecular reaction principle the slope value would be 33.2° C. or 59.8° F. Whether or not this rate obtains in milk may not yet have been determined. We shall refer to this curve as the "inactivation time curve".

A phantom inactivation time curve will result from a series of rate-of-inactivation curves at different temperatures. This curve will establish between different pasteurization processes relationships that correspond completely to those discussed for the curves shown on Figure 8. It will tell what process at 71.7° C. will accomplish the same degree of inactivation as the process of 30 minutes at 61.7° C. This process at 71.7° C. will not be the same as those at the same temperature which are equivalent to 30 minutes at 61.7° C. with respect to microorganisms of which the phantom thermal death time curves are different from the inactivation time curve for phosphatase. If the slope value of this curve is 33.2° C. (59.8° F.), 15 minutes at 71.7° C. will be equivalent to 30 minutes at 61.7° C. Thus, if processes are based upon an organism of which the phantom thermal death time curve

#### Table V. Lethality Values of Processes at 161° F. (71.7° C.)

 $(IT = 40^{\circ} \text{ F. or } 4.4^{\circ} \text{ C.}; g_e = 1^{\circ} \text{ F. or } 0.56^{\circ} \text{ C.}; l_H \text{ for each process when just adequate for pasteurization against the organism; p in per cent of adequate lethal heat in process when <math>l_H = ID$ 

Process No.	t R	Rate of Temp. Rise	le	Rate of Temp. Decline	<i>FT</i> , ° F.	<i>CW</i> , °F.	Br. $z = 0$ $U = 0$ $tH$	suis, 9.2° F. 9.32 p	S. aeriz = 18U = tH	rycke, .9° F., 3.34 P
1 2 3 4 5	0		0 15 7 15 7	A A D D	40 40 40 41 41	40 40	0.32 <0 0.098 0.189 0.259	100.0 249.0 169.4 141.0 119.1	3.34 2.32 2.87 3.08 3.22	100.0 130.5 114.1 107.8 103.6
6 7 8 9 10	15	A	0 15 7 15 7	A A D D	40 40 41 41	40 40	<0 <0 <0 <0 <0 <0	249.0 366.0 318.5 243.0 221.2	2.32 1.31 1.85 2.07 2.20	130.5 160.8 144.7 138.1 134.1
11 12 13 14 15	7	A	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	0.098 <0 <0 <0 0.022	169.4 318.5 238.8 210.3 193.0	2.87 1.85 2.39 2.61 2.75	114.1 144.7 128.4 121.9 117.7
16 17 18 19 20	15	B	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	<0 <0 <0 <0 <0	2146 2300 2220 2193 2174	<0 <0 <0 <0 <0	344.5 375.4 359.0 352.8 348.3
21 22 23 24 25	7	B	0 15 7 15 7	A A D D	40 40 40 41 41	40 40	<0 <0 <0 <0 <0	1056 1207 1126 1096 1075	<0 <0 <0 <0 <0 <0	214.4 245.1 228.4 222.3 218.0
26 27 28 29 30	15	C	0 15 7 15 7	Â A D D	40 40 40 41 41	40 40	<0 <0 <0 <0 <0	1163 1313 1232 1204 1183	<0 <0 <0 <0 <0	256.0 286.3 270.0 263.7 259.3
31 32 33 34 35	7	C	0 15 7 15 7	Â A D D	40 40 41 41	40 40	<0 <0 <0 <0 <0	600.0 702.8 667.0 640.6 617.8	0.912 <0 0.451 0.661 0.801	172.7 203.0 186.5 180.2 176.0

the processes may be responsible for the fact that an undue amount of credit seems to have been attributed to the temperature of 71.7° C., in considering that 16 seconds at that temperature are equivalent to 30 minutes at 61.7° C. A part of the lethal effect attributed to the holding time at 71.7° C. perhaps rightly belongs to the coming-up period. If so, a slope value greater than that of curve S, Figure 8, is indicated. It is true that the slope value indicated by data for Br. suis is very close to that of curve S. The available curve for Br. suis, however, is one of the less well defined curves. The three points given do not indicate it clearly. An additional fact bearing on the comparisons is that the data on S. aertrycke were made during a heat resistance test with the use of broth instead of milk.

#### **Phosphatase test**

Just as bacteria of a given strain are destroyed by heat in accordance with a timetemperature relationship shown by a thermal death time curve, the enzyme phosphatase undoubtedly is inactivated by heat in harmony with a somewhat similar pattern. Since phosphatase inactivation probably is more nearly a pure chemical reaction than is the destruction of bacteria, the reaction under certain conditions might proceed on the simple monomolecular reaction principle,

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differs from the phantom inactivation time curve for phosphatase, the degree of phosphatase inactivation for processes at different temperatures which have equal bacteriadestroying power will vary, and this variation will have to be taken into account if the phosphatase test is used as the criterion of adequate pasteurization. The degree of inactivation that indicates adequate pasteurization at 71.7° C. will not be the same as that which indicated adequate pasteurization at 61.7° C. The same principle applies to any other test of the sufficiency of pasteurization processes.

#### Summary

Experience in evaluation of canned foods processes, by demonstrating the importance of slope values of thermal death time curves, shows a way to obtain lethality values of pasteurization processes referred to that of the standard process of 30 minutes at 61.7° C. (143° F.). Phantom thermal death time curves, which have the same slope values as real thermal death time curves but have no definite positions, are used. An explanation is presented of two facts:

The comparative lethal values of two pasteurization processes at different temperatures depend upon the bacterial or chemical standards by which they are measured. The fact that two processes are equivalent on the basis of one standard does not signify equivalence on the basis of another standard.

2. The lethality value of the period during which the milk is brought to holding temperature, as well as the lethality value of the period of cooling, may be important when the process is short.

The efficacy of the pasteurization process of 30 minutes at 61.7° C. has been established by years of experience. Calculations based on the bacteria-destroying value of this process as a reference standard show the comparative value of processes at other times and temperatures in destroying different types of bacteria. On the basis of available data, 19.2 seconds at 71.7° C. has destructive power equivalent to 30 minutes at 61.7° C. for Br. suis; but for S. aertrycke a process of 3 minutes 20.4 seconds at 71.7° C. is required to have destructive power equal to that of 30 minutes at 61.7° C. These variations in equivalence with respect to different bacteria between processes at different temperatures are controlled by the slopes of phantom thermal death time curves for the bacteria.

This principle is important in a consideration of any test for proving the sufficiency of a pasteurization process, such as the phosphatase test. The slope value of the phantom inactivation time curve for phosphatase has an effect analogous to that of the slope values of phantom thermal death time curves for bacteria. Assuming that the enzyme phosphatase in milk is inactivated by heat at the monomolecular chemical reaction rate, one finds that for this test a process of 15 minutes at 71.7° C. will produce the same results as those by a process of 30 minutes at 61.7° C.

These equivalents are based on actual heating times at the given temperatures, with instantaneous rise to temperature and instantaneous cooling assumed. Periods of time consumed in heating the milk to holding temperature and in cooling the milk, along with the holding period at the pasteurization temperature, contribute to the destruction of bacteria and enzymes. When a rise of temperature to 71.7 ° C. proceeds over a period of 7 minutes and the cooling of the milk requires a similar length of time, the periods of rise and decline of temperature may contribute more lethal heat to the destruction of bacteria or to the inactivation of phosphatase than is contributed by the holding period of the process. The fact that only 16 seconds at 71.7° C. has been found to give adequate pasteurization indicates that the effects of comingup and cooling periods have been overlooked in the interpretation of the results of tests, as well as of commercial operations.

The bacteria-destroying values of processes having various combinations of rate of rise and decline of temperature show that these periods must be taken into account in the scientific evaluation and comparison of pasteurization process. For Br. suis a period of 7 minutes to bring the temperature of the milk to 71.7° C. could supply almost ten times as much lethal heat as is required to destroy the organism.

#### Acknowledgment

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Courtesy, Cherry-Burrell Corporation Milk Pasteurizer of Long-Hold Type, Spray-Vat Style

# Protection of natural green pigment in the canning of peas

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• • It has been found that the texture of canned peas is affected far more by cation exchange with the various solutions with which they are in contact during the canning operation than it is by variations of pH level within the median pH range. By a suitable choice of alkaline reagents applied in a definite sequence, it is therefore possible to maintain a normal canned-pea texture while elevating the pH sufficiently to protect about 60 per cent of the chlorophyll of peas against conversion to pheophytin. A moderate elevation of pH level has an effect on flavor which most observers consider to be favorable. The flavor effect is a reversible function of pH level and appears to be largely due to shifts in the dissociation of those odor-iferous natural constituents of canned peas which are weak acids or bases.

**NONVENTIONAL** canning procedures change the color of peas and of other green vegetables from the natural green to what is commonly termed an "olive" color. Willstätter has shown that the natural green pigment is the same in all higher plants and consists of a mixture of chlorophyll A, C<sub>55</sub>H<sub>72</sub>O<sub>5</sub>N<sub>4</sub>Mg, and chlorophyll B, C<sub>55</sub>H<sub>70</sub>O<sub>6</sub>N<sub>4</sub>Mg. The component magnesium of the chlorophylls is nonionic; it is carried by the pigment into solution in nonpolar solvents such as ether, and this property may be utilized for its analytical differentiation from the very much larger proportion of ionic magnesium which is always present in plant tissue. Willstatter showed also that retention of pigment magnesium in chlorophyll and its immediate derivatives is correlated with greenness. From his work it might be surmised that the primary step in the degradation of chlorophyll in canning is probably the loss of pigment magnesium in the hydrolytic conversion of chlorophyll to pheophytin:

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This paper includes direct analytical evidence, obtained with peas, that this assumption is correct. The loss of pigment magnesium in the conventional canning of peas is complete.

There is some evidence (10, 19) that in plant tissue chlorophyll is stabilized against acidic plant saps by compound formation of the pigment with protein. It may also be protected by physical segregation in the chloroplasts of the fresh, unaltered plant tissue. The protection afforded by such factors is lost during cooking, and therefore the only known factor available for the protection of natural greenness in canning green vegetables is the establishment of an alkaline environment. The earliest record, known to authors, of the effect of this factor is that of James Haigh (9) who in 1813 wrote:

Alkalies heighten the colour both of the tinctures and green juices (of leaves). Acids weaken, destroy, or change it to a brownish. Lime water improves both the colour and the durability. By means of lime, not inelegant green lakes are procurable from the leaves of acanthus, lilly of the valley, and several other plants. Joslyn and Mackinney (11) showed by an analysis of spectrometric results that the conversion of chlorophyll to pheophytin is of the first order with respect to hydrogen-ion concentration.

#### Early attempts to protect greenness

Apparently the earliest attempt to protect the natural green color of vegetables during canning was that described by Blassneck (6). In this procedure the vegetable is either soaked at room temperature or blanched at a higher temperature in a suspension of calcium hydroxide. It is specified that unabsorbed solid calcium hydroxide should be removed by washing before the vegetable is placed in the can. Blassneck considered that "the natural dye stuff of the vegetables... is fixed or set in the skin or pulp, before it can be altered by boiling". No mention of an effect on texture was made, except to say that "peas which are preserved according to this process are made less gelatinous".

Butler and Drumm (8) describe a procedure based upon the use of an "alkaline buffer solution". Sodium bicarbonate is mentioned, but disodium phosphate is specifically recommended. These authors stress the assumed necessity of using alkaline reagents which are "buffer salts". Thus they state: "We only use magnesium hydroxide in conjunction with an alkaline buffer solution. Magnesium hydroxide by itself is not a buffer solution and it does not accomplish the same result."

Sharma (25) describes the use of magnesium carbonate in canning green vegetables, particularly spinach. This reagent is recommended as one which is "mild enough in its action so that while readily neutralizing the organic acids of the vegetable it will not attack the tissue". The slight solubility of the reagent is considered as a further advantage because "any added amount over and above this value (i. e., that required for saturation) will simply remain in suspension without affecting the spinach in any way". It is stated that the magnesium carbonate may be added either to the brine with which the vegetable is canned, or to the water in which the vegetable is blanched. In the latter case it is stated that the vegetable

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may or may not be freed from excess reagent before it is placed in cans. Other alkaline earth carbonates are also mentioned as blanching reagents, and it is specified that these must be removed by washing after the blanch because of their toxicity.

Adam (1) describes the results of two years of experimental work with peas at elevated pH level. Adam appears to have taken it for granted, as did Butler and Drumm and also Sharma, that only a "mild alkaline reagent" or "alkaline buffer salt" could be used. Adam found it necessary to use sodium carbonate in 1.5 per cent or sodium phosphate in 8 per cent concentration to afford adequate protection to the green color of peas. The principal disadvantages which induced Adam to abandon the problem were an "alkaline flavor" and a softening effect on the peas. He states that the alkaline flavor "is unavoidable owing to the large quantity of alkaline buffer required", and that the softening of the peas took place "owing to the solvent action of alkaline solutions on the cellular structure".

None of the foregoing procedures appear to have been put into actual practice except possibly the procedure of Blassneck. Serger and Luchow (24) state: "The method of Blassneck seemed for a while to be giving results which showed the proper direction to follow. . . . The results were in general good, nevertheless the process has not attained great significance in Germany, because the flavor of the canned product was not always (einwandfrei) good."

#### **Outline of present procedure**

Work in this laboratory during the past seven years has shown that it is possible to retain approximately 60 per cent of the pigment magnesium, and hence a very satisfactory degree of greenness, in the canning of peas by a specific alkalizing procedure which gives a product whose texture approximates that of the same peas canned conventionally. An unanticipated result is that the flavor appears to be closer than that of the conventional canned product to the flavor of freshcooked peas. Experiments which afford a partial explanation of this flavor benefit will be discussed below.

This procedure has been developed as a result of a large number of empirical canning experiments in which a variety of alkaline reagents were used in different ways and at various molarities, until certain principles became evident which led to a specific procedure and the conclusions that rather rigorous adherence to this specific procedure is necessary. In evaluating the results of these experiments, the authors were guided by Munsell color comparisons and by an analytical method for chlorophyll, developed in this laboratory (2) and based on a microdetermination of pigment magnesium. Unfortunately, no really satisfactory method exists for the objective measurement of one of the most important factorsnamely, the texture of the canned peas. However, subjective evaluation of texture (the chewing test) by experienced observers is on the whole a safe guide, which was subsequently vindicated by the results of a rather elaborate application of the only recognized objective method (the "cotyledon crusher" of Bonney, Clifford, and Lepper, ?) to peas canned by the specific procedure in comparison with the same peas canned conventionally. The results of this experiment are presented below and constitute reasonably good evidence that the pH level can be elevated sufficiently to protect chlorophyll without altering significantly the texture of the final canned product.

The specific procedure arrived at by this experimentation comprises three major steps (5) as follows:

1. A pretreatment, involving the immersion of the peas at room temperature in 2 per cent (0.19 M) sodium carbonate solution for 30 to 60 minutes.

Blanching in a 0.005 M calcium hydroxide solution.

3. Processing the peak with a salt-sugar brine which is also a 0.020 to 0.025 M suspension of magnesium hydroxide.

Certain auxiliary practices must be observed, as follows:

It is essential that the blanch be adequate to inactivate the respiratory enzymes completely before the peas are filled into the cans, otherwise the acid products of their action will reduce considerably the pH level of the final product. If the peas are not blanched at all, this effect can amount to as much as one pH

Thorough but rapid surface washing of the peas after the pre-treatment and after the blanch is essential for uniformity of results and contributes materially to brine clarity in the final

results and contributes inacciany to brine charty in the final product. The use of lime-soda softened water, essentially free from bi-carbonate and carbonate ions, also contributes to brine clarity. The use of a "short-high" process, such as 7 minutes at 260° F. rather than the customary process (for peas in No. 2 cans) of 35 minutes at 240° F., is essential for satisfactory results. Peas given a 35-minute heat process at the higher pH level, although green, tend to be darker than when given the shorter process given a 35-minute heat process at the higher pH level, although green, tend to be darker than when given the shorter process. The darkening effect of a longer process is still more perceptible in the brine. On the other hand, the short-high process alone, without the establishment of an elevated pH level, is entirely in-adequate for the protection of chlorophyll in canning. Peas given the short-high process and otherwise conventionally canned will, it is true, have a tinge of greenpess immediately after ear will, it is true, have a tinge of greenness immediately after canning, but this slight greenness is rapidly lost in storage, even when the storage is at 40° F.

Peas canned by the specific alkalizing procedure described above will not lose appreciable greenness through many months of storage at 40° F. At 70° F. the color is reasonably stable, but at higher temperatures the loss of color is rapid. An experiment is described below in which the chlorophyll content was deteris described below in which the chlorophyli content was deter-mined as a function of duration and temperature of storage. Greater stability of greenness in storage can be attained at higher pH levels established by higher molarities of magnesium hydrox-ide in the brine, but excessively high alkalinity results in unfavor-able flavor effects (production of ammonia and hydrogen sulfide). Approximately 200 000 ages of page hous hous separad by

Approximately 300,000 cases of peas have been canned by this procedure during the past four years.

#### Principles of the procedure

The experience gained in the numerous exploratory experiments and in commercial practice can be summarized as follows:

PRINCIPLE 1. Alkaline reagents do not fix or set the color in the sense of altering the nature of the pigment in the direction of increased chemical stability. The language of Blassneck indicates that he was laboring under this misconception, which is perhaps not surprising in view of the early date of his work. Evidence will be presented below which indicates that a good part, at least, of the green pigment remaining after canning is unaltered chlorophyll, protected against hydrolytic decomposition only by the elevated pH of the environment. In checks of Blassneck's procedure, with peas, calcium hydroxide was used in a pretreatment and then thoroughly removed, as Blassneck specifies, before the product was placed in the can. The resulting canned peas were only slightly greener than the conventionally packed controls.

PRINCIPLE 2. A factor which must be taken into account is that a decrease in pH level is a characteristic accompaniment of the process of sterilization of almost any food by heat (3). The juice of raw peas ordinarily has a pH level close to 6.6, while the conventionally canned product generally approximates pH 6.1. In the procedure described above, the pH level within the peas themselves is established at about 8 in the first step (before heat has been applied), and maintained close to pH 8 through the blanching and sterilization steps by use of alkaline reagents in each step. Attempts to avoid the addition of an alkaline reagent as a constituent of the brine used in the last step, by more drastic treatment in the earlier stages, cause excessive disintegration, undesirable flavor change, and darkening of the product.

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PRINCIPLE 3. When the pH level within the peas is thus maintained within the median pH range throughout the whole canning operation, the softening effect of excessive alkalinity does not manifest itself. In the median pH range the controlling factor as to texture is not pH level but the cationic equilibria existing between the peas and the solutions with which they are in contact during the canning operation. The base-exchange property of plant tissue has been discussed by McGeorge (16), but its importance in determining texture appears to have been strangely neglected prior to the recent work of Kertész and coworkers (13, 22). Canners have long known that the use of hard water in canning peas causes them to be hard and tough (4), an effect which results from an increase in the calcium and magnesium content of structural (pectic) constituents of the peas. The reverse effect is shown by an experiment, discussed below, which shows that the calcium and magnesium content of peas is not decreased by extraction with cold water, but is markedly decreased by base exchange with a cold solution of sodium chloride. In further confirmation of this principle, experiments in this laboratory in which alkaline compounds of sodium (bicarbonate, carbonate, secondary phosphate, or hydroxide) were used exclusively throughout the canning operation have always given soft gelatinous peas and viscous starchy brines, thus confirming and explaining the observations of Adam. On the other hand, when Blassneck's reagent, calcium hydroxide, was not only used for blanching but was also placed in the can in sufficient amount to protect the color during the sterilization by heat, the peas had extremely tough seed coats and also firm cotyledons, the effect on the skins being greater than that on the cotyledons. Strangely enough, Adam did not recognize that the effect of the cation, and not the effect of alkalinity, is pre-



Courtesy, Berlin-Chapman Company

Rotating Bucket Blancher

This new type uses fresh blanching solution for each lot of peas and permits control of calcium hydroxide concentration in this step of the alkalizing procedure.

dominant in regard to texture, since he says "the softening effect . . . can be overcome to some extent by blanching in hard water, or by adding soluble calcium salt at this stage".

PRINCIPLE 4. The preconception that even the slight alkalinity necessary to protect greenness is the predominant cause of softening has been a stumbling block in the various attempts to develop a successful procedure. Butler and Drumm, Adam, Sharma, and the present authors in their early work were all so imbued with this idea that it was considered necessary to use buffer salts or mild alkaline reagents of one kind or another. Here again Adam came close to recognizing an essential principle, since he discusses the large buffer capacity of the peas themselves. Unfortunately his only conclusion was that it necessitated the use of a brine containing 1.5 per cent sodium carbonate or 8 per cent sodium phosphate, with the result that "the alkaline flavor . . . is unavoidable owing to the large quantity of alkaline buffer required". The present authors finally recognized that the peas have considerable capacity to do their own buffering, and that a principle essential to success is the use of the hydroxides (of the proper cations) in small concentration, rather than buffer salts in the high concentration in which they must be used to be effective. Peas brought to pH 8 by the proper use of a hydroxide definitely do not have an alkaline flavor, whereas peas whose pH level is elevated by buffer salts do have off-flavors which observers tend to describe as alkaline because of their mental associations but which are in reality the sodalike flavors of the foreign anions.

PRINCIPLE 5. It is true, however, that the use of hydroxides does require close control of concentration. The use of sodium carbonate rather than sodium hydroxide in the first stage of the specific procedure described above, is, in part, a

concession adopted for commercial practice in view of the critical importance of concentration when sodium hydroxide is used. An experiment is discussed below which contrasts these two reagents in regard to their effect on pH level within raw peas immersed in their solutions. Small experimental packs of peas have also been prepared using sodium hydroxide (in much smaller concentration) instead of sodium carbonate in the pretreatment stage. While the results were in general satisfactory, the comparable lots involving sodium carbonate in the pretreatment did seem to have a slightly better flavor after canning. It may be true, as a qualification to principle 4, that the "ceiling on pH level" afforded by the use of sodium carbonate for pretreatment is a definite advantage. In this connection it is believed that in a carbonate solution the hydroxyl ion produced by hydrolysis,

$$\mathrm{CO_{3}^{--} + H_{2}O = HCO_{3}^{-} + OH^{-}}$$

penetrates the peas much more rapidly than the carbonate ion itself; in fact there is some evidence that little carbonate is carried into the final product from the pretreatment solution but remains largely external to the peas and is removed in the washing operation after the pretreatment. As evidence for these statements the following observations can be offered:

Raw peas lose the gray opacity of their seed coats much more rapidly in a sodium hydroxide solution than in even a considerably more concentrated sodium carbonate solution.



Figure 1. Equilibrium pH Levels of Raw and of Blanched Peas with Sodium Hydroxide

Peas packed according to the specified procedure, using untreated or zeolite-softened water which contains bicarbonate ion, have a cloudy liquor due presumably to microcrystalline calcium carbonate. On the other hand, peas similarly packed using relatively carbonate-free (lime-soda softened) water, will have a clear liquor in spite of the presence of carbonate in the pretreatment solution.

**PRINCIPLE 6.** Magnesium hydroxide has two unique properties which render it indispensable as the alkalizing reagent for use in the brine:

Of all the cations suitable for use in a canning procedure, magnesium ion has the least effect on the texture of peas. The slight effect it does have seems to be in the direction of increased firmness.

Magnesium hydroxide is slightly soluble, and its solubility does not change greatly with temperature. If its solubility is taken as 0.009 gram per liter (23) or 0.00015 molarity, this reagent is theoretically incapable of raising the pH level of an aqueous system above pH 10.5, no matter how much excess solid magnesium hydroxide is present in suspension. This checks well with actual pH determinations of the brines used. In the brine suspensions specified in the procedure described above, about 99 per cent of the magnesium hydroxide is present in solid phase as an alkaline reserve, capable of entering into heterogeneous reaction with the peas to counteract the acidifying tendency of the sterilization by heat. A sodium hydroxide brine of comparable titratable alkalinity (0.05 normal) would have a (theoretical) initial pH value of 12.7. Due to the moderating influence arising from its slight solubility, magnesium hydroxide is entirely devoid of the deleterious effects presumably feared by Sharma in his recommendation of the use of magnesium carbonate. Magnesium hydroxide and magnesium carbonate as brine reagents have been experimentally compared by the present authors. Mole for mole, magnesium hydroxide is much more effective in raising the pH level and protecting the greenness of the peas. As a matter of fact, the present authors have found that one of the benefits of the use of line-soda-softened water as compared with zeolite-softened or untreated water in making up the solutions used in the above procedure is the greater effectiveness in line-soda-softened water of a given molarity of magnesium hydroxide, due to the absence of a given molarity of magnesium hydroxide, but othe absence of is asturated solution. Excess of either solid phase does not "remain in suspension" as Sharma thought, but enters into heterogeneous reaction with the vegetable tissue during the process of sterilization by heat. The value of the slight solubility of these two reagents is merely that it puts a "ceiling" on the initial pH

The statement of Butler and Drumm that magnesium hydroxide by itself does not accomplish a desirable result can only have been based upon incomplete observations.

PRINCIPLE 7. To avoid a possible misconception, it may be well to emphasize the fact that magnesium hydroxide protects greenness during canning solely because it is an alkaline reagent. Sodium, calcium, and magnesium hydroxides are approximately equal in effectiveness, at equal normalities, so far as the greenness of the canned product is concerned. The hydrolytic conversion of chlorophyll to pheophytin is irreversible in an aqueous system, as pointed out by Willstätter. Therefore, even though magnesium ion is a product of this reaction, the rate of the reaction is not subject to any mass-action effect of magnesium ion. The authors have carried out experiments which show that no restoration of greenness takes place when conventionally canned peas are recanned after magnesium hydroxide is added to their brines.

Thoroughgoing investigations by O. R. Alexander and J. M. Feaster of this laboratory have shown that there is no appreciable difference between peas canned conventionally and peas canned by the specified alkalizing proced-

ure as to vitamin content (thiamine and ascorbic acid). Their results will be presented in a separate communication.

# Equilibrium pH levels of raw and blanched peas with sodium hydroxide

When raw peas are comminuted with water or with a sodium hydroxide solution, the pH level drifts downward continuously due to production of acids by the respiratory enzymes of the peas. This precludes any attempts to determine a titration curve in the usual manner, when working with a raw pea slurry.

The data of Figure 1 were obtained with market peas of mixed sieve sizes 3, 4, and 5. Each determined point on each curve represents the pH level at ionic equilibrium between 25.0 grams of peas and 75.0 ml. of one of a series of standard sodium hydroxide solutions. The peas and solution were placed in a Waring Blendor which was operated for one minute (stop watch). An additional minute was required to determine the pH level in a glass-electrode cell. Temperatures throughout ranged from 21° to 25° C. The peas as obtained were divided into two equal portions. One portion was used raw (curves 1 and 2). The other portion was added to an equal volume of boiling water and kept submerged during the 6 minutes required for the water to reach boiling again (curves 3 and 4). The pH levels determined 2 and 60 minutes after the initial disruption of the raw and blanched peas are shown on Figure 1.

The results illustrate the considerable buffer capacity of peas and the large effect of the active enzymes of raw peas in lowering pH level. The absence of such an enzymatic effect in blanched peas is evidenced by the practical coincidence of curves 3 and 4 in the lower pH range; the falling off of curve 4 in the higher pH range may be due to absorption of carbon dioxide from the atmosphere by the highly alkaline systems during the 60-minute interval.

The results of this experiment indicate that peas exhibit less enzymatic activity when macerated with water (pH 6.7) than when an initial pH level of 8 to 9 is established by sodium hydroxide. The stimulation of the enzymatic activity of peas by an alkaline environment was noted by Zaleski (28).

In interpreting the results of this experiment it may be of interest to note that a brine 0.025 molar with respect to magnesium hydroxide, in the proportion customarily used (brine/pea ratio = 0.53) in packing succulent peas, corresponds to 2.65 milliequivalents of base per 100 grams peas.

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#### Relative rates of imbibition of sodium hydroxide and carbonate

Market peas, sieve size 4, were used for this experiment. Twenty-two 25.0-gram samples were weighed out and placed in the refrigerator to inhibit change. Each sample was covered with 50.0 ml. of either water or one of a series of standard solutions ranging up to 1.00 normal for sodium hydroxide and up to 2.00 normal for sodium carbonate. At the end of 30 or 60 minutes each sample of peas was drained and washed twice by decantation with distilled water (one minute) and comminuted in a Waring Blendor with 50 ml. of water (one minute), and the pH was determined by glass electrode (one minute). Work with the successive samples overlapped so that the elapsed time for the whole experiment was 150 The temperature of a typical system rose from minutes. 16° (cold peas and room-temperature water) to 21° after 30 minutes and 22° after 60 minutes.

The results are expressed in Figure 2. In carrying out the experiment it was obvious that the sodium hydroxide solutions penetrated the peas much more rapidly than the sodium carbonate solutions. In all but the two most dilute sodium hydroxide solutions, the peas during 30 minutes became intensely green, rather than gray-green and sank in the solutions; in all the sodium carbonate solutions the peas as a whole remained more or less gray and continued to float.

Unfortunately no experiment so complete as this was carried out with peas of fancy quality. However, such peas have been examined from time to time at the end of the 30-minute pretreatment (in approximately 0.4 N-sodium carbonate solution) of the specified procedure in commercial operation. These pH levels (after thorough rinsing of the peas) have ranged from 7.8 to 8.1. It is evident, therefore, that a sodium carbonate solution is considerably more effective in raising the pH level within succulent canning peas than within market peas such as were used in the experiment just described.

In accordance with the trend shown by this experiment, it has been empirically observed in practice that, when packing peas of large-seeded varieties (such as Profusions in which fancy quality is obtainable in sieve size 6), it is advantageous to prolong the pretreatment of the specified procedure to 60 rather than 30 minutes. No untoward effects are perceptible in such cases. With smaller peas, such as those of the Perfection variety, the 30-minute pretreatment is adequate.

Other experiments have shown that imbibition of the alka-





line reagent may be hastened by raising the temperature during the pretreatment. However, this results in definite offflavor in the final canned product, due presumably to accelerated enzymatic action. In practice the pretreatment is never carried out above 70° F.

Certain observations have indicated that the imbibition of the alkaline reagent may be accelerated somewhat by intermittent evacuation during the pretreatment. However, this work has not yet been carried to definite conclusions.

#### **Base-exchange extraction of calcium** and magnesium by sodium chloride

The base-exchange property of peas may be illustrated by an experiment on the extent to which the calcium and magnesium, naturally occurring in peas, could be extracted at room temperature by distilled water and by 5 and 10 per cent sodium chloride solutions. It was desired to use peas that had been blanched, and for convenience commercially frozen peas were chosen. In each case a 50-gram sample of peas was continuously shaken in a 500-ml. Erlenmeyer flask with 200 ml. of water or salt solution. This procedure was twice repeated using fresh portions of water or salt solution, so that each sample of peas was extracted for a total of 45 minutes with three successive portions of solvent. The averaged analytical results follow:

	Original	After 45-Min. Extraction with:				
	Peas	Water	5% NaCl	10% NaCl		
Magnesium, p. p. m.	504	485	313	227		
Mg retention, %	100	96	62	45		
Calcium, p. p. m.	240	248	192	164		
Caretention, %	100	103	80	68		

These data are subject to an undetermined error corresponding to whatever change may have taken place in the weights of the pea samples during extraction.

#### Nature of green pigment

The following observations, taken together, indicate that the green pigment present in peas canned by the specified alkalizing procedure is probably chlorophyll itself:

The pigment retains its component magnesium (2). An ether extract of the pigment gives the "brown phase reac-tion" (27). The brown phase was considerably less intense than that given by a pigment extract from fresh peas. Nevertheless, the reaction was unmistakably positive and indicates that some of the green pigment in the canned peas is not even allomerized. The absorption surface surface are in the source of the source of the source of the source source source of the source sour

The absorption spectrum curve of a pig-ment extract of peas canned by the specified alkalizing procedure is intermediate in character between that of an unaltered extract of fresh peas and that of an extract of fresh peas in which the chlorophyll has been converted to pheophytin by acid treatment. On the other hand, the absorption spectrum curve of a pig-ment extract of conventionally canned peas is similar to the pheophytin curve. The results of an experiment which establishes these facts are presented in Figure 3.

The principle of this method is that of Mackinney and Weast (18), which was based on the theory of Joslyn and Mackinney (11). In this work, however, the pigments of the pea samples were obtained in ether solution by the present authors' method (2) for determining pigment magnesium. The washed ether solutions were evaporated to dryness and taken up in chloroform. These chloroform solutions were used in the spectrophotometric work instead of the 90 per cent acetone solutions of Mackinney and Weast. The latter used oxalic acid to convert chlorophyll to pheophytin for standardizing purposes; in the present work trichloroacetic acid was used. The photoelectric spectrophotometer employed was constructed in this laboratory and will be described elsewhere  $(\mathscr{D})$ .



Figure 3. Absorption Spectra of Pigment Extracts in Chloroform l = 5.08 cm.; S. R. l. = 100 Å.

The results are presented in Figure 3, which corresponds to Figure 1 of the paper by Mackinney and Weast. Curve 1 represents the absorption spectrum of a pigment extract of fresh peas, while curve II represents the absorption spectrum of a second aliquot of the same extract after conversion of the chlorophyll to pheophytin. These two curves intersect at 554 instead of 560 millimicrons as found by Mackinney and Weast under their experimental conditions. Curve IV represents the "corrected" absorption of a pigment extract of conventionally canned peas; it resembles, but is not exactly coincident with, the pheophytin curve. Curve III represents the "corrected" absorption of peas canned by the specified alkalizing procedure; its position between curves I and II gives credence to the postulate that in this sample something like half of the chlorophyll remained unchanged.

The corrections of curves III and IV were applied as described by Mackinney and Weast in converting their curve IIIA to their curve III. The actual curve for conventional peas was parallel to our curve IV but passed through point C at 554 millimicrons, while the actual curve for peas canned by the alkalizing procedure was parallel to curve III but passed through point A. As explained by Mackinney and Weast, these corrections are made necessary by the fact that the original chlorophyll content of the samples under examination is not the same as that of the sample used for establishing the standardizing curves, I and II.

#### Destruction of chlorophyll and lowering of pH level

PROCEDURE. This experiment was carried out with freshly harvested canning peas of the Alderman variety, sieve size 5 and fancy quality. The fill (315 grams blanched peas and 167 ml. brine, both accurate within one per cent) was packed in 303  $\times$  406 C-enameled cans. The 5-minute blanch was carried out in No. 10 cans in a steam blanch box, the temperature reaching 200° F. A time schedule was worked out to equalize holding periods for all lots throughout the pack. On account of the inevitable holding periods, the peas were cooled in ice water after blanching, and the brines were added and the cans closed at room temperature. The commercial practice of filling and closing hot is not achievable in a quantitative experimental pack of this magnitude without incurring greater errors than those which may arise from cold closure.

The data of the experiment are given in Table I. Reacting systems before processing are represented by letters A to I, reacting systems after heat processing by numbers 1 to 27. The whole experiment was carried out in duplicate; each symbol therefore represents two samples. The pH values (glass electrode) are represented by ordinary roman type; the chlorophyll values, in parts per million, are expressed by italics.

The pH values of the raw and blanched peas were determined on slurries obtained by macerating the rinsed peas with an approximately equal volume of water. The pH values representing the other experimental conditions were obtained with the brine phase. The values obtained with the two samples representing each experimental condition agreed within 0.05 pH unit except for system 23. In this case an extreme discrepancy unaccountably occurred, the two values being 7.74 and 8.13. The latter value is so far out of line that it is believed to be in error. The pH values given for the reacting systems before processing (A to I) were made after exactly 10-minute contact between blanched peas and brine at room temperature. After this interval the brines were drained from the peas in order to stop the heterogeneous reaction between peas and brine at that point. In the case of the processed samples, the retort was blown down and the cans were placed in ice water within 30 seconds of the end of each process. A few minutes thereafter the cans were opened, the brines drained off for pH measurement, and the peas held for chlorophyll analysis according to the method described below.

All the brines were made with distilled water, contained 2.16 per cent salt and 3.00 per cent sugar, and had other properties as follows:

Nominal Molarity Mg(OH):	Titrated Molarity	pH
Plain brine		5.57
0.01	0.0102	10.01
0.02	0.0201	10.06
0.03	0.0300	10.08

The titrated alkalinity of the alkaline blanch corresponded to 0.0065 M calcium hydroxide.

The values for chlorophyll content are based on the method for determining pigment magnesium, which will be described in a separate communication (2). The weight of a given lot of peas is considerably affected by blanching, processing, etc., and it was desired to have the chlorophyll results on a raw pea basis. Therefore, the pea-count method recommended by Kertész (12) was adopted. Forty-five of the raw peas used were found to weigh from 24.68 to 25.38 grams in eight determinations. Every sample therefore consisted of forty-five peas, whatever the stage of the canning procedure, and the chlorophyll result was calculated on the basis of a 25-gram sample. The counted samples of raw, pretreated, and blanched peas were covered with a 2 per cent sodium carbonate solution (to stabilize the chlorophyll) and placed on ice as fast as they could be obtained in the course of the experiment. At the end of the packing experiment these systems were frozen, held at  $-15^{\circ}$  F. overnight, and carried through the critical stages of the analytical procedure the next day. In the case of the processed lots, the peas from the cans opened shortly after processing were covered with 2 per cent sodium carbonate and held just above freezing until they could be analyzed. Four days were required to work up all the samples, but the samples which had received the shortest processes were analyzed first.

The values given for chlorophyll are the averages of four or six values, corresponding to duplicate or (in most cases) triplicate aliquots of the duplicate samples. The maximum deviation from the mean did not exceed 6 per cent except in (Er

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	Alkalizing	Pretrestment (	() Only, after Wa	Fresh raw shing 8.0	peas, pH 6.59 6; Alkalizing l	, 114 p. p. m. ch Pretreatment and	llorophyll) I Blanch, 7.73, 1	02	Conventional E	Blanch, 6.61, 102
Agita	ted 270° F. I	Process, 1-Min. 0.010 M	Come-up 0.020 M	Process		Stationary 0.010 M	260° F. Process 0.020 M	s, 4-Min. Come 0.030 M	-up	0.030 M Mg(QH)3
time,	Plain brine	Mg(OH): brine	Mg(OH): brine	min.	Plain brine	brine	Mg(OH) <sub>2</sub> brine	brine	Plain brine	brine
0ª 3.5 4.5 5.5	A, 7.77 1, 7.30 4, 7.22 7, 7.18, 63	<b>B</b> , 8.69 2, 7.93 5, 7.89 8, 7.84, 75	C, 8.82 3, 8.33 6, 8.29 9, 8.22, 79	0ª 4 6 8	D, 7.80 10, 7.32 16, 7.23 22, error in brining	E, 8.65 11, 7.97, <i>81</i> 17, 7.90, <i>82</i> 23, 7.74, <i>66</i>	F, 8.81 12, 8.38, 87 18, 8.30, 74 24, 8.21, 66	G, 8.89 13, 8.62, 87 19, 8.59, 76 25, 8.68, 77	H, 6.74 14, 6.48 20, 6.39 26, 6.36, <i>28</i>	<b>I</b> , 8.71 15, 8.36 21, 8.29 27, 8.18, <i>5</i> 4

the case of sample 26, for which six values were obtained ranging from 24 to 31 p. p. m. chlorophyll.

RESULTS. Processing at 260° F. was included because this temperature is the highest feasible for stationary retort (still-cook) operation. Experience has shown that under such conditions the processing temperature cannot be reached in less than 4 minutes. Bacteriological evidence obtained in this laboratory has shown that 7 minutes at 260° F. following a 4-minute "come-up" is adequate for commercial sterilization in No. 2 cans. Processing at 270° F. with a 1-minute come-up and an agitated cook (in a Fort Wayne sterilizer) was included in the experiment as an approximation to procedures that would be feasible if continuous cookers were made available to pea canners. Preliminary heat penetration data, in conjunction with bacteriological data, showed that, after their respective come-up periods, 3.5 minutes at 270° F. is bacteriologically equivalent to 4 minutes at 260° F.; 4.5 minutes at 260° F., to 6 minutes at 260° F.; and 5.5 minutes at 270° F., to 8 minutes at 260° F.

It is to be noted that, in this experiment, bacteriologically equivalent processes give the same pH level. Thus, lot 9 has the same pH level as lot 24, etc. However, it is doubtful whether this generalization would hold if extrapolated to lower temperatures, and may represent a particular situation in the heterogeneous reaction rather than any very fundamental chemical principle. The particular point of interest is illustrated by the fact that the peas of lot 9 have a higher chlorophyll content than the peas of lot 24, in spite of the congruity in pH level. The same effect is brought out by comparing lot 8 with lot 23. In other words, the destruction of chlorophyll is not the same kind of function of time and temperature as the decrease in pH level.

The benefits conferred by the alkaline pretreatment and blanch are brought out by comparing series 13-19-25 with series 15-21-27.

Magnesium hydroxide at 0.01 molarity just compensates for the acidifying effect of an 8-minute process at 260° F., since the pH level of lot 23 is the same as that of the peas entering the cans after an alkaline pretreatment and blanch.

The results of this experiment seem to show that peas contain as much chlorophyll after the conventional blanch as after the alkaline pretreatment and blanch; the chlorophyll content being 102 p. p. m. in both cases. This was an unexpected result, since peas after the alkaline pretreatment and blanch are always greener in color than after the conventional blanch. Conversion to unallomerized isochlorophyllin might be suggested in explanation of increased greenness unaccompanied by an increase in pigment magnesium content. This possibility is, however, discounted by the fact that the green pigment of peas canned by the specified alkalizing procedure is insoluble, not only in the alkaline brines but also in the strongly alkaline aqueous wash solutions used in our analytical method for pigment magnesium.

Perhaps the most likely explanation of this anomaly in re-

gard to the relative greenness of the two types of blanched peas lies in an extraction of yellow flavone pigments in the alkaline pretreatment. After draining from the peas, this solution sometimes has a slightly yellowish cast. On the other hand, peas seem to contain very little flavones as compared to other green vegetables. No well-established explanation of the anomaly can be offered at present.

# Uniformity of pH level shortly after processing

In the conventional canning procedure, applied to peas of uniform character, very little inter-can variation in pH level is encountered after processing. This is to be expected, since the salt-sugar brines used in the conventional procedure are totally unbuffered; and the peas, as modified by a constant heat-treatment, are the sole factor affecting pH level.

It is more difficult to obtain a uniform pH level in canning peas packed by the specified alkaline procedure. The molarity of magnesium hydroxide in the brine must be kept constant, and its suspension in the brine must be kept uniform by constant agitation. In practice, all three alkaline solutions used in the procedure are checked by titration. The attempt is made to keep the brine-pea ratio constant by uniform filler operation.

The heterogeneous system probably does not reach ionic equilibrium until some hours after canning. In the preceding section it was pointed out that the pH level immediately after canning, with the magnesium hydroxide at 0.020 molarity,

Table II. pH Survey of a Day's Pack at a Cannery

Batch No.	Titrated Brine Molarity	Sample No.	pH a	after:
A	0.0207	1 2	7.73	7.61
В	0.0210	1 2	7.77	7.70
С	0.0210	1 2	7.82	7.84
D	0.0203	1 2	7.96	7.70
E	0.0215	1 2	7.82	7.77
F	0.0202	1 2	7.39	7.29
G	0.0217	12	8.03	7.79
н	0.0217	12	7.93	8.00
I	0.0217	12	7.96	7.55
J	0.0215	1 2	7.88	7.83
K	0.0215	1 2	7.70	7.69
L	0.0214	1	7.69	7.90
М	0.0206	1 2	7.92	7.84
N	0.0213	1	7.61	7.71
0	0.0208	1	7.80	7.71
		Averag	;e 7.78	7.71

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Months of Storage	32° F.	45° F. Chloroph	p. Contro 55° F. nyll Cont	olled Appr 65° F. ent, P. P.	75° F. M.	y at: 85° F.	95° F.
1 2 3 4 6 8 10	58 56 45 58 55 51 45	59 58 50 59 43 39	58 52 55 46 40 27 24	50 42 31 25 13 14 10	39 20 14 13 7 4	27 11 9 3 1	13 6 0 2
		1	Average r	H Values	3		
1 2 3 4 6 8 10	7.79 7.71 7.74 7.82 7.78 7.65 7.59	$\begin{array}{c} 7.78 \\ 7.80 \\ 7.74 \\ 7.74 \\ 7.66 \\ 7.46 \\ 7.71 \end{array}$	$\begin{array}{c} 7.65 \\ 7.66 \\ 7.71 \\ 7.49 \\ 7.60 \\ 7.62 \\ 7.47 \end{array}$	$\begin{array}{c} 7.80 \\ 7.55 \\ 7.47 \\ 7.48 \\ 7.51 \\ 7.36 \\ 7.51 \end{array}$	$\begin{array}{c} 7.56 \\ 7.33 \\ 7.53 \\ 7.30 \\ 7.49 \\ 7.43 \end{array}$	7.56 7.33 7.51 7.33 7.20	$\begin{array}{c} 7.31 \\ 7.17 \\ 7.26 \\ 7.05 \\ 7.11 \end{array}$

Table III. Effect of Storage Time and Temperature on Chlorophyll and pH

was 8.2. Some hours after canning, the pH level at this molarity is generally about 7.8.

The results of a pH survey of an entire day's pack at one cannery are presented in Table II, together with the titrated molarities of each brine used. There brines were made from lime-soda softened water, the alkalinity of which corresponded to a 0.0012 M diacidic base.

The peas were Profusion variety, of mixed sieve sizes 5 and 6, and were adequately blanched. The duration of all pretreatments was 30 minutes, and all other conditions were reasonably constant as specified above for the standard alkalizing procedure. Two samples of each batch were examined 12-24 hours and two other samples 36-48 hours after processing. No clean-cut correlation between pH level and brine molarity is apparent in Table II, which is evidence of the importance of other factors difficult to control. Nevertheless, an increase in brine molarity to about 0.023 will result in an increase of average pH level to about 8.0. A maximum of 0.025 molarity (which has no perceptible bad effects) has been used in practice, but the 0.023 molarity is generally adequate, while the 0.020 molarity is to be regarded as the minimum compatible with reasonable stability of greenness in storage.

# Effect of temperature and storage time on chlorophyll content

The storage factor has been investigated in an experiment initiated in 1938. Extra Standard Perfection peas, sieve size 4, were packed according to the specified procedure using a 0.020 M magnesium hydroxide brine. This pack was stored for 10 months at seven temperatures (32°, 45°, 55°, 65°, 75°, 85°, and 95° F.) in a graded thermostat; spaced metallic compartments were insulated from the room and from one another except that they were clamped to a bank of thermally conducting bars which extended from an ice bath at one end to a thermostatically controlled oven at the other. This worked well during cool weather when the room containing the apparatus was maintained at 70° F., but during the summer there was a decided hump in the temperature gradient so that the intermediate compartments were as much as 5° F. above their nominal values. This occurred during the first 2 months of the experiment, and should be taken into account in interpreting the results. Our other experience indicates that chlorophyll is in reality more stable at 65° and 75° F. than would be apparent from the results in Table III.

Another defect in the experiment is the considerable degree of inter-can variation. This is evident by discrepancies encountered in the pH levels of duplicate cans. The inter-can variations are due to the fact that a rather large pack was required, and one of us had to do it by hand since the procedure was not yet in commercial operation. This involved long holding periods, variations in rinsing, and undoubted "slips" in the control of brine/pea ratio in filling the cans. Our analytical method for chlorophyll was not so fully developed as it became later, but the internal evidence of the experiment indicates that the chlorophyll method was the source of less error than the variations between samples.

The fresh raw peas used in the experiment contained 99 p. p. m. chlorophyll. At the initiation of controlled storage, which was about 2 weeks after canning (at 0.020 brine molarity) the peas contained 58 p. p. m. chlorophyll, and the pH level was 7.77.

The worst discrepancy between chlorophyll values of duplicate samples was encountered after 6 months at 32° F. where 55 p. p. m. is an average between 47 and 62 p. p. m. (Table III). In two other cases duplicate values differed by 8 p. p. m. In all other cases the agreement was better than this.

The worst discrepancy between average pH values of duplicates was encountered after 6 months at  $95^{\circ}$  F., where 7.11 is an average between 6.95 and 7.27 (Table III). In twelve other cases the discrepancy was more than 0.1 unit, which may be considered as permissible error in pH measurement. It it more likely that these discrepancies are due to inter-can variations in packing than to variance between duplicates in changes during storage.

In spite of its imperfections, this experiment indicates that the pH level decreases in storage at a rate which is a function of temperature. This is unquestionably a factor which accelerates the loss of chlorophyll in warm storage. However, the results of the experiment show that chlorophyll would be lost even if the pH value were constant, at a rate which is itself a function of temperature. These results on chlorophyll



Courtesy, Clyman Canning Company Stainless Steel Pretreatment Tanks

Each tank is equipped with a valve with two ports; one port is equipped with a screen through which used solution is drained, the other then admits the peas to the conveyor. 10

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in canned peas are thus in agreement with the conclusions of Mackinney and Joslyn (17), based on their work on isolated chlorophyll in aqueous acetone solution.

#### Effect of alkalizing on calcium and magnesium contents

An elaborate analytical investigation of canned peas, including peas canned by the specified alkalizing procedure, has been carried out by the Analytical Division of this laboratory, under the supervision of O. R. Alexander. The results will be presented in a forthcoming paper. The present paper will include, therefore, only a brief summary of the calcium and magnesium data obtained in a single controlled experiment.

Fancy Alderman peas, sieve size 5, were used. After conventional blanching, it was found that 315 grams of peas (the standard fill for a  $303 \times 406$  can) comprised 655 peas. All samples, including the raw peas, therefore consisted of 655 peas, and the results are computed on a 315-gram sampleweight basis. Five lots were involved. The experiment was carried out in triplicate. The average values are presented in Table IV, which also shows the percentage increment of each lot as compared with the original raw peas.

#### Table IV. Effect of Alkalizing Procedure on Calcium and **Magnesium Contents of Peas**

	0	alcium	Magnesium			
Peas	P. p. m.	% increment	P. p. m.	% increment		
Lot A <sup>a</sup> Lot B <sup>b</sup>	250 219	-12	385 295	-23		
Drained peas only Peas and brine	175 229	$-30 \\ -8$	199 302	-48 - 21		
Lot D <sup>d</sup> Drained peas only Peas and brine	253 312	$^{+1}_{+25}$	254 369	-34 -4		
Drained peas only Peas and brine	223 255	$-11 \\ +2$	407 568	$^{+6}_{+48}$		

b Peas after pretreatment of specified procedure, rinsed with distilled

vate:
 Peas packed conventionally using distilled water throughout.
 Peas packed conventionally, using hard water containing 71 p. p. m.
 easim and 44 p. p. m. magnesium.
 Peas packed by specified alkalizing procedure using distilled water throughout

The results show that if the consumer discards the brine and uses the drained peas only, the specified alkalizing pro-

cedure gives him the nearest approach to the calcium and magnesium content of the raw vegetable. Lot B, in comparison with lot A, measures the base-exchange loss of calcium and magnesium during the sodium carbonate pretreatment.

#### Cotyledon texture

The only recognized method for determining objectively the texture of canned peas is that described by Bonney, Clifford, and Lepper (7) which measures the total force required to crush an individual cotyledon to one fourth its original thickness, when the initial force of 100 grams is augmented at the uniform rate of 12 grams per second. Strictly speaking, this method is applicable only to the definition of canned peas as substandard when more than 10 per cent by count of the peas require a total force of 907.2 grams or more to crush them under the stipulated conditions.

In the endeavor to obtain peas of substandard grade for this experiment, a lot of Perfection peas of sieve size 5, obtained the last day of the 1941 packing season, were put through a flotation grader and only the "sinkers" in an 11.8 per cent salt solution were used. The peas were packed by three procedures (Table V).

Six cans of each lot were examined, each can being represented by one hundred individual peas. The individual readings were classified into eight categories as to crushing force. These results show the tremendous pea-to-pea variation in cotyledon texture within each can, and the considerable discrepancies between the six cans of each lot. It seems safe to conclude that there is no real evidence of significant differences in texture between the three lots.

It may be reiterated that seed-coat texture is not a factor in this experiment since the peas were peeled and only the cotyledons used.

#### Effect of elevated pH level on flavor

The following facts have been established by blindfold flavor comparisons of peas canned by the specified alkalizing procedure, with control lots of the same peas canned conventionally, using the same short-high heat process in both cases:

Peas canned at the higher pH level have a sweeter-seeming flavor than when canned at the conventional pH level, so that it is desirable to use about 30 per cent less sugar in the brine than is customary in the conventional procedure. A slight relative sourness is perceptible in the conventional pack, and it is believed that the difference in apparent sweetness is merely the result of the psychological balancing of sweetness against sourness, just as a lemonade requires less sugar if the acidity is partially neutralized.

Peas packed conventionally have a stronger, sharper, and more acrid odor than peas packed at the higher pH level. This differ-ence in odor is a never-failing characteristic. With few exceptions, observers say that peas canned at the higher pH level are characterized by an odor that is a closer approach to the aroma of This has been attested to even by observers who state that through usage they have come to prefer conventionally canned peas to fresh peas. Such observers generally prefer convention-ally canned peas to peas canned by the specified alkalizing procedure.

The difference in flavor and aroma between conventionally canned peas and those canned by the specified alkalizing procalled peak and those called by the specified arkalizing pro-cedure is, in large measure at least, a reversible function of pH level. We may say that the pH level of peas packed conven-tionally is typically 6.1, and that of peas packed by the specified alkalizing procedure is typically 7.6. When conventionally

#### Table V. Effect of Alkalizing Procedure on Cotyledon Texture

			Per	Cent or rea	as Ci usileu	Dy rouce	free cos marine)	01.	Over
Lut	Sample	0-299	300-399	400-499	500-599	600699	700-799	800-907	907
A ª	1 2 3 4 5 6	23 29 25 25 16 11 22	23 26 21 18 21 15 21	12 14 19 22 17 17	6 9 8 5 10 15 9	8 9 4 8 9 11 8	7 3 2 6 6 6 5	5 6 3 4 3 6 5	16 5 18 12 18 19 15
Bø	1 2 3 4 5 6 Av.	20 25 16 13 10 3 15	29 24 24 11 10 5 17	15 21 26 23 10 9 17	15 14 14 22 16 15 16	13 9 9 15 16 19 14	4 5 0 6 9 8 5	2 1 3 6 13 13 6	2 1 8 4 16 28 10
Ce	1 2 3 4 5 6	27 20 32 24 21 20	27 22 24 32 17 21	11 16 23 25 19 14	9 13 16 6 16 15	10 6 2 5 13 9	5 2 0 2 9 11	5 6 1 3 2 2	6 15 2 3 3 8
	Av.	24	24	18	13	8	5	3	6

Declined attaining proceeding, processing 7 minutes at 260° F.
 Conventional procedure, processing 35 minutes at 240° F.

packed, peas are puréed in a Waring Blendor with their brine and the pH of the purée is raised to 7.6 by adding a few drops of concentrated sodium hydroxide solution, blindfolded observers identify the purée as one made from peas packed by the alkalizing procedure. When a purée is similarly made from peas packed at the elevated pH level, and the pH level is lowered to 6.1 by a few drops of concentrated hydrochloric acid, blindfolded observers identify the purée as one made from conventionally packed peas.

It is believed that the reversibility of flavor and aroma as a function of pH level affords the key to the major part of the flavor difference between the two styles of pack. Further evidence is afforded by the results of experiments applying to canned peas the technique of König and coworkers (14, 15) who worked with carrots, cabbage, apples, and asparagus in the fresh, cellar-stored, or dried condition.

König passed oxygen-free nitrogen through these food products (puréed) at temperatures slightly above 100° C. The stream of nitrogen was then led through a series of receivers filled with ammoniacal silver

solution. With this as a basis König was able to identify, and estimate quantitatively, carbon dioxide, hydrogen sulfide, methyl mercaptan, formaldehyde, acetaldehyde, and butyraldehyde as volatile constituents of all these foodstuffs. The aldehydes are oxidized by the ammoniacal silver in the receiver to the corresponding acids, which are the substances actually determined. It may be suggested, however, that some part of the carboxylic acids found by König may have occurred as such in their plant materials. This possibility is not ruled out by König's procedure.

The original silver precipitate obtained in the König procedure includes metallic silver (mirror), silver sulfide, and silver methyl mercaptide. König found that 5 per cent hydrochloride decomposes silver mercaptide but not silver sulfide. He therefore digested the original silver precipitate with 5 per cent acid and distilled it into alkaline hydrogen peroxide which converted the mercaptan to sulfate, determinable as the barium salt. The undecomposed silver residue was then treated with concentrated hydrochloric acid; hydrogen sulfide was liberated and was estimated in the same way.

In the present work a variation of König's procedure was applied to puréed canned peas in four experiments. In ammoniacal silver a brownish-black precipitate was obtained, with evidences of silver mirror just as described by König. In working up the silver precipitate, however, reliable qualitative evidence as to the presence of mercaptan in canned peas was considered more important than its quantitative estimation. Therefore, in our work the original silver precipitate was treated with 5 per cent hydrochloric acid under a current of nitrogen which led through ammoniacal silver. Very little warming was required. A dull yellow precipitate, entirely free from black silver sulfide, was formed in the receiver. When washed, this precipitate had a perceptible "rotten cabbage" odor of methyl mercaptan; and when acid was added to a few crumbs of it, the odor became powerful. A known sample of methyl mercaptan, added to water in the König apparatus, gave an identical-appearing yellow precipitate which was entirely decomposable by 5 per cent hydrochloric acid. The residual silver precipitate from the peas, undecomposed by 5 per cent acid, was then treated with concentrated hydrochloric acid under a current of nitrogen again leading through ammoniacal silver solution. A copious black silver sulfide was formed. These experiments establish the fact that



#### Figure 4. Dissociation Residue Curves

peas, as well as the foodstuffs investigated by König, yield both hydrogen sulfide and mercaptan on heating slightly above 100° C.

Peas were among the plant products found by Rubner (21) to yield methyl mercaptan on fusion with solid potassium hydroxide, but in view of König's work and our own it is evident that mercaptan is formed from plant tissue, presumably by hydrolysis of methionine (26), under much less drastic conditions than those of Rubner.

The significance of this work is that methyl mercaptan and hydrogen sulfide typify the odoriferous constituents of peas that are weak acids. The intensity of such odors is enhanced at low pH and decreased at high pH levels because of the fact that only the undissociated acid, and not the ion or ions thereof, has an odor. To be odoriferous a substance must be lipoid soluble (20) and must also have a certain vapor pressure. Hydrogen sulfide and methyl mercaptan have both of these properties; their ions have neither.

To test this experimentally, methyl mercaptan was added to each of a series of five buffers ranging from pH 3.7 to 9.5, to form solutions in which the mercaptan concentration was 1 p. p. m. None of the solutions were odorless, but there was a definite inverse correlation of odor intensity with pH level. A solution of 1 p. p. m. methyl mercaptan in normal sodium hydroxide is nearly odorless.

An attempt was made to ascertain whether peas contain weakly basic odoriferous constituents. Such substances would be enhanced in odoriferous intensity in peas canned by the specified alkalizing procedure as compared with peas canned conventionally. For this purpose a König experiment was carried out in which the receiver containing ammoniacal silver was followed by one containing 0.35 N sulfuric acid. On subsequently neutralizing this odorless solution, there is liberated (besides ammonia) a nasturtium- or geraniumlike odor which has not been identified. The same odor was obtained when a steam distillate from canned peas was shaken out with ether, the ether solution extracted with acid, the acid neutralized and again extracted with ether, and the final ether solution evaporated.

It is possible to think about such flavor factors in quantitative terms when the dissociation constant is known, as it is in the case of hydrogen sulfide. The total concentration [S] of sulfide,  $[S] = [H_2S] + [HS^-] + [S^{--}]$ , will depend, in a can 127

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15 mil 22 of peas, on the raw material and on the extent to which such substances as cysteine have been hydrolyzed during the canning procedure. The authors have no evidence to offer as to the relative effects of the two canning procedures discussed here on the total sulfide concentration, but believe that they do not greatly differ in this respect so long as the alkalizing procedure stays properly within the median pH range. If this is granted (provisionally), then the intensity of sulfide odor will depend on the concentration of undissociated hydrogen sulfide, which may be expressed as  $[H_2S] = [H_2S]/[S] \times [S]$ , where the ratio [H<sub>2</sub>S]/[S] is the dissociation residue, and is a unique function of the pH level existing within the can of peas and the dissociation constant of hydrogen sulfide:

D. R. (of an acid) = 1/[1 + 10 (pH - pKa)]

For a weak base the converse relation holds:

D. R. (of a base) =  $1/(1 + 10 (pK_{ab} - pH))$ where  $pK_{ab} = pK_w - pK_b$ 

These relations are shown graphically in Figure 4. Thus hydrogen sulfide should have 89.7 per cent of its maximum odor intensity at pH 6.1, taken as typical for conventionally canned peas, but only 21.6 per cent of its maximum odor intensity at pH 7.6, taken as typical of peas canned by the specified alkalizing procedure. The carbonate system is certainly present in all canned vegetables; the curve shows that conventional canned peas will be the more "carbonated" and alkalized peas, the more "sodalike" in flavor. The curve for ammonium hydroxide shows that it is so strong a base that the rapidly descending part of the dissociation-residue curve falls outside the median pH range, which is of interest in comparing the two types of canned peas. Therefore the concentration of undissociated ammonium hydroxide should be low, and an ammoniacal odor should not be perceptible in either type of canned peas, properly packed. Aniline is included in Figure 4, not because there is evidence that it occurs in any foodstuff, but merely to illustrate the situation with respect to an extremely weak base. An odoriferous substance so weakly basic would be highly odoriferous at either pH 6.1 or 7.6.

It is true that the odor of hydrogen sulfide as well as ammonia is perceptible when peas are packed at excessively high pH levels. This can be due only to an extremely high concentration of total sulfide [S], more than sufficient to compensate for the low dissociation residue at high pH level.

These considerations are discussed at some length because their importance in the flavorful effects of canning is not confined to peas. Experiments in this laboratory have shown that with certain other vegetables, such as carrots, lima beans, and asparagus, the flavor is also improved by raising the pH level of the canned product. So far as the present authors are aware, it has not been recognized hitherto that the universal lowering of pH level, which accompanies the conventional canning of almost all vegetables, may be a causative factor in flavor changes in canning.

#### Acknowledgment

This development is the result of a collaborative effort involving the aid of numerous other members of the Research Department, under the constant and liberal encouragement of its administrative officers. This aid is gratefully acknowledged. Thanks are also due to John Albright, N. J. Lau, M. S. Canaday, and W. G. Glascoff for their interest and cooperation, and for making available for experimentation the facilities of their respective canning establishments.

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Courtesy, Trumbull Electric Manufacturing Company Milk-Pasteurizer of Short-Hold Type, Electro-Pure Design Employing Heat by Electrical Resistance (See article on page 71.)

# Fruit and vegetable juice preparation and preservation

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• • During the past decade the fruit and vegetable juice industry has increased fifty fold. The introduction of flash pasteurization and the perfection and general use of enamel-lined cans have been largely responsible for the remarkable growth of the industry. Heating to approximately 160° F. destroys all microorganisms in fruit juices except mold spores, which will not grow in the absence of air, and an occasional heat-resistant spore former which will not multiply in a medium having a pH of 4 or lower.

Recently fruit juice blends, such as orangegrapefruit and apple-raspberry, have been

THE continued expansion of the fruit and vegetable juice industry during the past twelve years has been amazing. A decade ago bottled grape juice and canned tomato juice were the only ones preserved on a large scale. At that time the tomato juice industry was still in its infancy. Today the list also includes grapefruit, pineapple, orange, apple, apricot, and lemon juices. In addition many other juices are being packed on a moderately large scale. Cherry, berry, pear, plum, rhubarb, sauerkraut, carrot, celery, and many other juices, either straight or blended, are canned or bottled. Statistics indicating the annual production of fruit juices (excluding tomato) and of tomato juice are summarized graphically in Figure 1 (19).

The great expansion of the industry is due partly to the recognition by the public of the nutritive value of fruit and vegetable juices and partly to increased demand caused by the marked improvement in quality of the commercial packs. Several factors are responsible for this improvement in



Figure 1. Annual Production of Canned and Bottled Fruit Juices and Tomato Juice

quality: Most packers no longer consider juices as by-products and now use first grade fruits and vegetables in their preparation; corrosionresistant enamels have been perfected for lining cans used for certain fruit juices; blends of both fruit and vegetable juices offered. These and other blends may become popular.

Both canned and bottled fruit juices retain flavor and color better when stored under refrigeration than when held at ordinary room temperatures. Much less tin is dissolved at low temperatures.

Vegetable juices, acidified either with lactic, citric, or phosphoric acid or with the juice of acid vegetables or vegetable products, may be preserved by flash pasteurization at approximately 185° F. Blends of sauerkraut juice with other vegetables have been found to be pleasing beverages.

have been introduced; and the advantages of deaeration and flash pasteurization and the general application of improved procedures in preparing and preserving fruit juices have been discovered.

#### Fruit juices

As long ago as 1920, Chace (4) suggested flash pasteurization as a method of preserving orange juice. More recently the procedure has been combined with deaeration and otherwise improved for use with orange juice (10, 11, 13).

In the early days of the pasteurized apple juice industry, great care was taken to clarify and filter the juice prior to pasteurization. This procedure improved the appearance of the juice; it also eliminated undesirable sedimentation and reduced the changes in flavor which occurred during holding pasteurization. Clarification, however, has the disadvantage of removing some of the apple flavor. Recently, it has been found that ordinary unclarified apple juice can be preserved by flash pasteurization without either appreciable change in flavor or deposit of sediment (16). Consequently, much flash-pasteurized apple juice is now being canned and bottled without clarification.

As now applied to apple juice (17) the procedure involves merely the following steps: straining the freshly pressed juice; deaeration; rapid heating in a tubular water-jacketed heat exchanger to 170° F.; filling (without cooling) into bottles or enamel-lined cans, taking care to fill each container completely; closing, inverting for a few minutes, and cooling. The pilot plant used at this station in research on flash pasteurization of all kinds of fruit juices is shown in Figure 2. Commercial scale equipment of this type is now used in many plants for the preservation of all kinds of fruit juices.

Yeast and bacteria which cause fermentation and spoilage of fruit juices are easily killed merely by heating to 140-150° F.

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The rate of destruction of microorganisms during the heating of cherry juice is shown in Table I. These data were obtained by making bacterial counts at half-minute intervals on cherry juice which was being heated in the inner compartment of a double boiler. Data obtained similarly during the heating of raspberry juices is presented in Table II.

In commercial practice the fruit juices are flash-heated to 170° F. or even higher for the following reasons: Microorganisms are not instantly killed, and in flash pasteurisation it is necessary to use somewhat higher temperatures. There is a possibility that certain types of organisms may be present which are relatively heat resistant. Enzymes are not rapidly inactivated at temperatures below 170° F., and if the enzymes are not destroyed during pasteurisation, the juice may develop off-flavors during storage. When the juice is run into the containers it is cooled slightly; it must still be sufficiently hot to obtain destruction of the microorganisms in the cans or bottles.

Mallory perfected special equipment (Figure 3) in which the heat treatment is truly a flash pasteurization. According to the Mallory "no-film" process, the juice is pumped under about 375 pounds per square inch pressure at high speed

Table I.	Plate Cou	nts to Show	« Killing o	f Microorganism
	·		the frame	Sour Cherries

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	duri	ng Paste	urizatio	n of Juie	e from 3	sour Che	rries
Time of Min.         Temp. ° F.         Plate count per cc.         Temp. of juice, ° F.         Plate per cc.         Temp. count ° F.         Plate count per cc.         Temp. of juice, per cc.         Plate of juice, per cc.         Temp. of juice, ° F.         Plate count per cc.         Temp. ° F.         Plate count per cc.         Temp. ° F.         Plate per cc.         Temp. ° F.         Plate count per cc.         Temp. ° F.         Plate count per cc.         Temp. ° F.         Plate count per cc.         Temp. ° F.         Plate count per cc.         Temp. ° F.         Plate per cc.         Temp. ° F.         Plate count per cc.         Count per cc.           0         69         40,000         72         50,000         124         25,000           1.5         111         40,000         128         145         b           2.5         145         8°         148         1°         153         580           3         153         0         158         4°         163         164         167         2b           4         163         1°         168         0         167         2b         174         0           5.5         170         0         175         2°         181         3 b           6         175		Montn Cold-I	ressed	Montr Hot-l	norency Pressed	Mo Hot-F	rello 'ressed
$ \begin{smallmatrix} 0 & 69 & 40,000 & 72 & 50,000 & 89 & 25,000 \\ 1 & 117 & 25,000 & 111 & 40,000 & 124 & 25,000 \\ 1.5 & & 126 & 15,500 & & \\ 2.5 & 145 & 8^{\circ} & 148 & 1^{\circ} & 153 & 580 \\ 3 & 153 & 0 & 153 & 0 & 158 & 4^{\circ} \\ 3.5 & 160 & 0 & 159 & 1^{\circ} & 165 & 1^{\circ} \\ 4 & 163 & 1^{\circ} & 164 & 0 & 167 & 2^{\circ} \\ 4.5 & 168 & 0 & 168 & 0 & \\ 5.5 & 170 & 0 & 172 & 0 & 174 & 0 \\ 5.5 & 173 & 0 & 175 & 2^{\circ} & 181 & 3^{\circ} \\ 6 & 175 & 0 & \\ \end{smallmatrix} $	Time of Ieating, Min.	Temp. of juice, F.	Plate count per cc.	Temp. of juice, F.	Plate count per cc.	Temp. of juice, F.	Plate count per cc.
6 175 0	0 1.5 2.5 3.5 4.5 5.5	69 117 138 145 153 160 163 168 168 170 173	40,000 25,000 610 8* 0 0 1* 0 0 0	72 111 126 140 148 153 159 164 168 172 175	50,000 40,000 15,500 282 1 <sup>a</sup> 0 1 <sup>a</sup> 0 0 0 2 <sup>a</sup>	89 124 145 153 158 165 167 174 181	25,000 25,000 580 4° 1 <sup>b</sup> 2 <sup>b</sup> 0 3 <sup>b</sup>
	6	175	0				

\* Aerobic spore-forming bacteria that will not grow in juice, • Mold present.

through a stainless steel tube of small bore surrounded by steam under pressure. In a second or two the juice is heated to 212° F. or even higher. After two or three seconds at this temperature, the juice passes to the cooling section of the apparatus which is similar in construction to that used for heating the juice. In this case cool water is employed in the outer compartment. In the cooling coil the juice is reduced to a temperature of about 170° F. at which it is filled into bottles or cans. The Mallory process works satisfactorily at temperatures far in excess of those which may be employed in flash pasteurizing juices in ordinary heat exchangers. Two reasons which may be advanced to explain this are the following: The juice is at the maximum temperature for only two or three seconds. The juice passes through the tube at such a high rate of speed and under such pressure that a stationary film of juice does not adhere to the inside of the tube; consequently, the juice does not take on a "cooked" flavor.

The Thermal Engineering Corporation has perfected equipment for the rapid heating and cooling of canned juices.



Figure 2. Experimental Deaerator (Two-Stage) and Flash Pasteurizer Used in Fruit and Vegetable Juice Studies

Using this equipment it is possible to obtain a product comparable in quality to that obtained by flash pasteurization methods. The rapid heat transfer is brought about by the rapid rotation of the cans as they are being passed through a long tank filled with sprays of water.

Ayers developed a unique system for the rapid sterilization of juices (1). In this patented Stero-Vac process the juice is flash-heated in the can in the substantial absence of air. This is accomplished by steam injection through a valve in the end of the can. This valve contains a floating disk which, after steam injection, is forced against a special sealing compound and crimped into permanent position and then tightly locked.

#### Fruit juice blends

A blend of grapefruit and orange juices has been on the market only a short time, yet a considerable volume is being sold. The success of this product will pave the way for other citrus juice blends.

Some juices—e. g., Montmorency cherry, raspberry, and plum juices—are too strong in flavor to appeal to many persons. These juices may be diluted with weak sugar sirup. The product—e. g., "cherry cocktail"—is a pleasant beverage, but it is no longer a fruit juice and does not have the

Table I	I. Plate	<b>Counts</b> to	Show F	Killing o	of Micr	oorganisms
	during	Pasteuriza	tion of	Raspbe	erry Ju	ices

	Red Ra	spberry,	Black R Hot-Presse	aspberry, ed, pH 3.58	Pur Rasp	ple berry
Time of Heating, Min.	Temp. of juice, F.	Plate count per cc.	Temp. of juice, F.	Plate count per cc.	Temp. of juice, F.	Plate count per cc.
0 1 2 3 4 5 6 7 8 9 10 12 14 16	$\begin{array}{c} 52\\ 70\\ 88\\ 104\\ 118\\ 126\\ 133\\ 141\\ 146\\ 150\\ 154\\ 160\\ 165\\ \end{array}$	9000 5000 5000 3500 242 a 3 <sup>a</sup> 0 0 0 0 0 0	$\begin{array}{r} 48\\ 64\\ 82\\ 97\\ 106\\ 109\\ 125\\ 133\\ 138\\ 142\\ 146\\ 153\\ 157\\ 160\\ \end{array}$	Moldy 510 124 108 80 33a 21a 9a 3a 0 0 0 0 0 0 1	68 64 118 125 132 138 143 143 143 151 159 165 172 180	8,000 5,000 5,200 5,000 2,800 76 0 1 e 6 e 1 e

<sup>b</sup> Aerobic spore-forming bacteria that will not grow in the juice.

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Figure 3. Mallory No-Film Sterilizer

proper body (viscosity). Experimental work at this station has shown that a blend of apple and cherry juices in the proportion of approximately 1 to 1 is superior in flavor to cherry juice diluted with sugar sirup of the same total solids content (2). A blend of approximately 3 parts apple with 1 part raspberry juice has become a popular beverage (14). Plum juice (2 parts), prepared from fresh Italian prunes, blended with Baldwin apple juice (1 part) is also excellent. The recommended amounts of apple juice and sugar to be added to various juices are shown in Table III. Of course these proportions should be varied to suit each individual lot of juice. In general, a larger proportion of apple juice can be used with hot-pressed than with cold-pressed juices.

Table III. Approximate Amoun Sugar Added to Fruit	t of Apple Juice Blends	Juice and
Fruit Juice	Apple Juice Added, %	Sugar Added, %
Strawberry, Dreaden Strawberry, Premier Grape, Concord Raspberry, black and purple Raspberry, black and purple Cherry, Montmorency Cherry, Montmorency and Schmidt Plum, Italian prune	$\begin{array}{c} 60.0 \\ 47.5 \\ 50.0 \\ 75.8 \\ 76.1 \\ 45.0 \\ 50.0 \\ 37.0 \end{array}$	5.0 5.0 0.0 3.9 1.0 3.0 0.0 1.5

79.7

3.3

Elderberry

The method used in making the apple-raspberry juice is somewhat different from procedures employed heretofore. When raspberries are pressed without heating, the resultant juice is relatively pale in color and its flavor is changed because of the action of oxidative enzymes. If the raspberries are heated and then pressed, the product has a strong flavor because of the solution of the tannins, etc., in the hot juice.

To obtain a deep red color without a strong flavor, the raspberries are frozen with 10 per cent added sugar (14). In the autumn when good juice apples are available, the berries are thawed and pressed immediately. Yields average 67 per cent for the black and 71 per cent for the purple raspberries. The pomace is warmed to 140–150° F. with an equal quantity of freshly pressed apple juice and pressed again. By this second extraction the yields from the black and purple raspberries are raised to about 71 and 77 per cent, respectively. Enough apple juice is added to bring the proportion of apple to raspberry to approximately 3 to 1. The blend is a little too tart, and some sugar may be added. Freezing prior to extraction is recommended for raspberries, strawberries, cranberries, plums, and cherries. Many pulpy fruit juices or nectars are on the market. If clarified, many of them would have little flavor—e.g., apricot, peach, and pear juices (S). A pulpy apple juice is now being offered. This is prepared by means of a Schwarz comminutor, then deaerated and flash-pasteurized. The product has a milky appearance but possesses a good apple flavor.

#### Changes during storage of fruit juices

Although juices are preserved by pasteurization as far as spoilage by microorganisms is concerned, certain reactions take place during subsequent storage. Ascorbic acid may be slowly lost, and the flavor and color of the juice may weaken or change in character. The rate at which these reactions occur is influenced by the temperature at which the juices are stored. Investigations carried on at the U.S. Citrus Products Stations showed that canned orange juice will retain its flavor almost indefinitely when stored at 32-35° F., but for only 2-3 months when stored at 75-85° F. (18). Work done at this station on other juices has shown similar results (15). Red raspberry juice stored at 33° F. for 4 months had a color in Lovibond units of 19.7 red and 7.1 yellow; the same juice stored at 86° F. showed only 9.2 red and 3.3 yellow. Similarly, strawberry juice stored at 33° F. for 3 months had a color of 9.7 red and 7.0 yellow; at 70° F., 5.2 red and 8.0 yellow, and at 86° F., 5.3 red and 12.6 yellow. The ascorbic acid content of the juice immediately after bottling was 0.35 mg. per gram. After 3 months' storage at 33° F. it was 0.31 mg. per gram, and when stored at 86° F. for the same time, was 0.21 mg. per gram. Of all these juices, those stored at 33° F. still had good flavor at the end of the storage period, while those at the higher temperatures were unsatisfactory.

Storage temperature also affects the rate at which cans are corroded by juice. This is shown by studies with apple juice. Freshly pressed juice (pH 3.4, total acidity 0.67 per cent malic acid) from the same lot of apples was deaerated, immediately flash-pasteurized at 175° F., and canned in five different types of cans (two enamel-lined and three plain tin). The product was stored at 40-50° F. for the first 2 months; then the lots were split. One portion was left at the original temperature and the other stored at 86° F. The experiment was completed at the end of 6 months. Analyses for iron and tin were made at 1, 3, and 5 days; 1, 2, 3, and 4 weeks; and then monthly. The amounts of tin found are shown in Figure 4.

At the end of the storage period approximately twice as much tin was found in juice stored at 86° F. than in similar



Figure 4. Tin Content of Canned Apple Juice

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cans held at  $41-50^{\circ}$  F. For example, can 5 (plain tin can) at  $86^{\circ}$  F. contained 45.7 p. p. m. of tin as compared to 21.7 when held at  $41-50^{\circ}$  F. As was to be expected, the amounts of tin in juice in plain cans was much larger than that in lined cans. In all cases the higher temperature caused an upward trend in tin content.



Figure 5. Comparative Effect of Hydrochloric (1), Lactic (2), Acid of Sauerkraut Juice (3), and Phosphoric (4) upon the Hydrogen-Ion Concentration of Beet Juice

The enamel-lined cans held at high temperature for 6 months were the only ones that showed increases of iron in the juice, having, respectively, 13 and 30 p. p. m. of iron. All other samples showed 2.5-4 p. p. m. of iron.

At the completion of the experiment the juices were given a final organoleptic examination. The juices from all containers stored at 41-50° F. were found to be better than any of those stored at 86° F. When the containers are held under identical conditions, enamel-lined cans are more satisfactory containers for apple juice than plain tin cans; but the juice packed in plain tin cans and stored at  $41-50^{\circ}$  F. was better than that packed in enamel-lined cans and held at 86° F.

Since changes in color, flavor, and ascorbic acid content of juices may be inhibited by storage at temperatures lower than those normally used, it is felt that more use should be made of refrigerated storage if the quality of canned juices is to be maintained.

# Improvement by acidifying vegetable juices

Most canners are not aware of the many advances made in the past few years in processes for fruit juices which may be used in the preservation of vegetable juices. As first produced, vegetable juices were processed for long periods at high temperatures. The temperatures employed were essential to preservation of juices of almost neutral reaction. This cooking caused undesirable flavor changes in the juice as well as excessive coagulation with resultant poor appearance. Products of a more acid nature do not require this high-temperature processing because the organisms are not only more readily killed, but also spore-forming bacteria that survive are unable to grow in an acid medium. Studies have been conducted at the University of California to note the effect of acidification upon the quality of the product (5, 7, 8, 12). These workers acidified with citric as well as hydrochloric and phosphoric acids, and concluded that the juices could be very pleasing if not too acid. Graham suggested the blending of nonacid vegetable juices with either acid fruit or acid vegetable juices or both (9). He proposed blending carrot and Table IV. Plate Counts to Show Killing of Microorganisms during Pasteurization of Carrot and of Carrot-Sauerkraut Juices

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Time of heating, min.	-Carrot Juice- Temp. of juice, °F.	Plate count per cc.	Carrot- Plate count per co.	Sauerkraut Temp. of juice, F.	Juice Time of heating, min.
	0 1:00 1:45 2:30 2:45 3:20 4:00 5:50 8:50 11:30	78 106 128 138 145 151 158 171 183 189	$53,000 \\ 48,000 \\ 55,000 \\ 1,550 \\ 70 \\ 80 \\ 17^{a} \\ 17^{a} \\ 13^{a} \\ 6^{a} \\ 6^{a}$	$27,000 \\ 33,000 \\ 9,400 \\ 3,100 \\ 19 \\ 16 \\ 14^{a} \\ 8^{a} \\ 5^{a} \\ 3^{a} \\ 3^{a}$	$78\\106\\114\\126\\138\\144\\149\\154\\173\\183\\188$	$0\\0:40\\1:15\\2:30\\2:45\\3:00\\3:25\\5:45\\8:55\\11:15$

other vegetable juices with citrus juices and processing the canned product in boiling water. Cruess and Chong also acidified carrot juice by blending it with orange juice and obtained a pleasing beverage which can be pasteurized at a low temperature (6).

We have felt that juices might be acidified with naturally acid vegetables such as rhubarb or with vegetable products such as sauerkraut juice. Or the necessary acidity might be produced by fermentation of the juice with lactic acid bacteria. The taste of rhubarb juice is so intense that the flavor of the vegetable is entirely lost. This is not true with sauerkraut juice, in that ordinarily the vegetable juice masks the flavor of the kraut juice. Further, it adds salt, essential to bringing out the flavor of a vegetable.

Comparison of the amounts of hydrochloric, phosphoric, and lactic acids required to adjust the acidity of a vegetable juice shows that, on a normality basis, hydrochloric is most effective, followed by lactic and then phosphoric (Figure 5). If calculated on a weight basis, the phosphoric is relatively more active. The acid of sauerkraut juice is primarily lactic, but if sauerkraut juice is used, considerably more acid is required to adjust the hydrogen-ion concentration (Figure 5). This buffering action of the kraut juice not only requires the addition of more acid but also reduces the sharpness of the resultant blend and produces a more pleasing product.

An adjustment of acidity to pH 4.0-4.1 is necessary to produce a blend of sufficient inhibitive nature to stop the devel-

# Table V. Comparative Buffer Action of Vegetable Juices

Vegetable	H-Ion Concn., nH	Cc. of 0.1 N Acid <sup>a</sup> 100 Cc. Juice to C 4.00	Required per hange pH to: 3.75
Celery	5.976.076.055.966.11	56.8 60.3 62.0 37.2 69.0	102.0180.9116.068.0136.0
Carrot	$\begin{array}{c} 6.44 \\ 6.21 \\ 6.31 \\ 6.48 \\ 6.02 \end{array}$	$\begin{array}{r} 41.6\\ 164.8\\ 124.1\\ 108.8\\ 94.0\\ 28.6\end{array}$	54.0 191.4 168.0 46.0
Beans Cabbage Onion Beet Beet	$\begin{array}{c} 6.19 \\ 6.07 \\ 5.50 \\ 6.38 \\ 6.26 \end{array}$	113.4 - 106.0 62.4 66.0 170.8	$200.0 \\ 134.0 \\ 126.0$
Turnip Rutabaga Spinach Peas Peas	5.80 6.07 6.18 6.77 6.65	52.0 62.0 81.6 177.1 162.7	108.0 108.0
a Lactic acid of sau	erkraut juice en	pressed as 0.1 N.	

opment of spore-forming bacteria, which in the past have caused spoilage in various food products. Where such a blend is pasteurized, temperatures required for killing bacteria are approximately 10° F. lower than in the case of nonacidified juices (Table IV). Further, it should be noted that spore-forming bacteria are not entirely killed in juices, whether or not they are acidified. The important difference, however, lies in the inability of the organisms to grow in the acidified juice. Curves show that pasteurization can be conducted at much lower temperatures than 185-190° F. The data indicate this, but spoilage types, such as lactic acid bacteria, are present in relatively low numbers, and heating to approximately 165° F. is required for complete killing.

The amount of acid necessary to obtain blends with a hydrogen-ion concentration of pH 4.0-4.1 varies considerably, not only with the vegetable used but also between different samples of a single vegetable (Table V). The quantity of kraut juice to obtain a pH of 4.00 varies from 37.2 to 69.0 cc. for celery juice, 28.6 to 164.8 cc. for carrot juice, and 28.6 to 170.8 cc. for all juices.

The blends of sauerkraut juice with vegetable juices have, in general, been far more appetizing than the straight vegetable juices. Furthermore, they may be blended with tomato juice in various proportions to produce pleasing tomato juice cocktails. Celery, carrot, beet, and turnip blends have been particularly satisfactory.

Juices have ordinarily been extracted from the fresh vegetable; and if the blend could not be prepared immediately, the juice was rapidly heated to 185-190° F. in order to inactivate the enzymes which would quickly cause a change in flavor, color, and vitamin content. Blanching previous to extraction may inactivate the enzymes more rapidly, but this treatment changes the character of the vegetable so much that the extracted juices are not so satisfactory.

Flash pasteurization at 185–190° F. preceded by deaeration, filling into bottles or cans at the above temperature, followed by cooling after 5 minutes has been found to be an effective means of preserving these blends without changing their flavor. The same equipment used for fruit juices (Figure 2) is satisfactory for the deaeration and flash pasteurization of either acidified vegetable juices or blends of vegetable juices with sauerkraut or rhubarb juice.

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# Acid detergents in food sanitation

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• • • Heretofore acid compounds have been unacceptable as cleaners because of their inferior detergency as well as their definitely corrosive action upon the metals used in constructing food processing equipment. The discovery of organic acids with relatively low corrosiveness and inherent inhibiting effects upon the quality-defective types of microorganisms first pointed the way to developing acceptable types of acid cleaners.

The effective combination of such acids with surface-active agents and corrosion retarders has resulted in the development of acid cleaning compounds possessing a detergency superior to that of most alkaline products, as well as providing an incidental wash water treatment, both corrective and curative, for the problem of water-stone and other calcareous formations. Therefore, acid cleaners promise not only a revision but an even greater improvement in the sanitary practices of food industries.

TERETOFORE the intelligent application of cleaning agents has involved a consideration of certain primary and secondary factors. The primary factors have been concerned with the chemical character of the water supply used in the cleaning operations as well as the degree and type of uncleanliness of the equipment. The secondary factors have implicated the availability of the alkalinity of the detergent used, the temperature and period of exposure, the proper application of the cleaning solution, and the thoroughness of applied mechanical action.

Alkalies and alkaline buffer salts have been almost exclusively used as detergents for several reasons. First and January, 1943

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山田 1 200 foremost from the standpoint of public health, they are nontoxic. They are also effective detergents although they do vary in their emulsifying, peptizing, wetting, and dispersive properties; for example, trisodium phosphate is superior to soda ash as an emulsifier of milk fat and peptizer of protein, while the poly-phosphates are not only superior to both, as regards such characteristics, but have wetting and dispersive properties lacking in the other two alkalies

Recent developments, however, have indicated that alkalies can no longer claim pre-eminence as effective detergents. In fact, in the light of more modern knowledge there is much evidence to suggest that alkaline compounds are responsible for many of the quality failures in present-day sanitary practice. An illustration occurs in can washing; there is an overwhelming abundance of evidence to indicate that the familiar 5-, 8-, and 10-gallon milk or cream can is most frequently a source of serious and far-reaching quality defections in a variety of dairy products.

Investigation has revealed that most mechanically cleaned cans have an unmistakable inoculation of proteolytic and oxidizing types of bacteria, and that such microorganisms are found most abundantly in the cans cleaned last in the day's run whenever alkaline cleaning compounds were used. Further studies indicate that these bacteria were being developed in the cleaning solution in spite of temperatures as high as 170° F. and a definite alkalinity as strong as 0.25 per cent (as Na<sub>2</sub>O)

As the day's operation continues, sufficient protein accumulates in the can washer to increase the film-forming properties of the cleaning solution. The film thus formed appears to cling to the metal surface in spite of the subsequent hot water and steam rinses and the hot air blasts. It also

retains the undesirable proteolytic bacteria and protein food material for the bacteria in sufficient concentration to make trouble if the can becomes moistened before it is again filled with milk or cream. In fact, sometimes even dry cans inoculate the milk with bacteria which impart bitter and often stale flavors to the fresh cream or milk poured into them.

Test runs showed that sterilizing steam having an acid reaction would correct this condition by releasing the colloidal film of cleaning solution with its bacterial contamination and nutrients generally adhering to the metal surface of the can, by greatly increasing the sterilizing action of the steam itself, and by leaving the inner surface of the can in an acid condition. The apparent effect of the treatment is that no appreciable concentration of protein material or proteolytic bacteria re-

#### Table I. Effect of Acid Reaction on Cleaned Cream Cans Rinsed with Steam Acidified with Citric Acid

Car		Bacterial	Count	Colony	Reaction
No.a	Can Reaction	Standard plate	Proteolytic	Acid	Alkaline
10 67 8 9	Acid <sup>b</sup> Acid <sup>b</sup> Alkaline <sup>c</sup> Alkaline <sup>c</sup> . Acid <sup>b</sup>	80 60 360 270 3	30 30 190 80 0	50 30 20 0 0	30 30 340 270 3
11	Alkalined Cleaning soln.	35 1	2 1	0 Appar all	35 ently all caline 145
	Rinse water "	180 stad at the start of	the day's run:	cans 5,	6, 7, and 8

Cans 9 and 11 were tested at the start of the day s run; cans 3, 6, 7 rere tested later, after operations had been underway for a few hours.
 Sweet odor in moist can held overnight.
 Putrid odor in moist can held overnight.
 Dirty unclean odor in can held overnight.
 Sample taken after cleaning 400 cans.
 / Too many bacteria colonies to count.

mains, as was repeatedly demonstrated by (a) no development of offensive odors in a moistened can, (b) a preponderance of acid types of bacteria in exhaustive microbial examinations of washed cans given this final acid rinse, and (c) the incidental reduction in the total numbers of bacteria originally present.

# Rinsing with organic acids

In preliminary plant trials citric acid was used because it was the only organic acid with which we were sufficiently familiar at the time to try out the original can acidification treatments. While it was known to be slightly corrosive, it is not nearly so undesirable as the mineral acids in this respect. A 0.5 per cent solution of citric acid was supplied to an ejector valve attached to the last steam jet on the can washer.



Spraying Previously Cleansed Coil Pasteurizer Vat with Acid Cleaner Solution (Replacing Chlorine Rinse Solution) to Prevent Contamination by Quality-Defective Microorganisms

When the steam jet was opened, the velocity of the steam sucked up the acid solution and mixed it with the steam to change the reaction of the steamed can from alkaline to acid. The amount of acid mixed with the steam was controlled by a valve in the suction line. To see if the cans were properly acidified, a can was rinsed with 50 cc. of distilled water, and the reaction of the water was determined colorimetrically with bromothymol blue indicator. A reaction of pH 6.0 to 6.5 wasfound to be adequate.

The comparative data in Table I indicate that acidulating the steam with a citric acid solution sufficient to change the reaction of cleaned cream cans from alkaline to acid resulted not only in significant changes in the types and numbers of the bacteria present but also in the odor of the treated cans. They were held overnight after adding 100 cc. of sterile water to moisten the inner surfaces. Incidentally, 1-cc. dilutions of the 100 cc. of sterile water used for checking the cleansed cans of both acid and alkaline reactions were plated immediately after their delivery from the can washer on standard tryptone-glucose extract-milk (T-G-E-M) agar and incubated for 48 hours at 37° C. The plates were then counted and the totals reported as standard plate count. Colonies surrounded by a clear zone indicating proteolysis of the milk were reported as proteolytic count. The plates were then flooded with bromothymol blue indicator solution, and the reaction was noted and reported as numbers of acid or alkaline colonies. In this manner general types were identified and reported.

The bacteria in the solution appeared to be either proteolytic or alkali forming in spite of the pH 10 alkalinity and 140° F. temperature. The 170° F. rinse water also showed a positive count of proteolytics and alkali formers.

Table II.	Chemical Anal Washer during	lysis of Cle Operation	aning So (Per Cer	lution i 1t)	in Can
Sample	Alkalinity (as NaOH)	Milk Fat	Protein	Total Solids	Ash
Fresh solution After 320 cans After 607 cans	a 0.25 a 0.22 a 0.29	$0.00 \\ 0.18 \\ 0.34$	Trace 0.03 0.18	$0.49 \\ 0.54 \\ 0.74$	0.11 0.20 0.16

After 400 cans had been run through the washer, the cleaning solution itself gave such a high bacterial count that an analysis was made of it at different intervals during the day's run to see what chemical changes were taking place. The results are given in Table II.

Data in Table II gives evidence that the accumulation of fat

and protein increased with the number of cream cans washed and provided nutrients for the surviving bacteria. The variations in alkalinity and ash can be explained on the basis of solution dissipation and dilution. However, the marked increase in total solids, protein, and fat in the sample taken after cleaning 607 cans with the decreases in alkalinity and ash reported seem to indicate that the milk fat or protein complexes formed by reaction with the alkali present contribute to colloidal film formations in the cleaned cans.

<sup>a</sup> Used for shipping sour cream.

It is true that the problem of corrosion has to be met. By acidifying steam with suction injection of gluconic acid in controllable quantities, the can is given an acid reaction of approximately pH 6.0 to 6.5, with no active corrosion of the can. Subsequently this method of acid rinsing has been tried in a variety of dairy plants with noticeable improvement in the quality of raw milk and cream transported in these mechanically cleaned cans.

In a special report of the Technical Committee of the Dairy Industry Supply Association (2), it was suggested that the acid rinsing of washed cans might tend to the development of careless production practice. Nothing could be farther from the original purposes of such a development, and clearly points to a common misconception which might be resolved when the microbiology and biochemistry of can washing and other similar dairy cleaning practices are ignored. It might be well to emphasize that the improvements in can washing during recent years are essentially the result of good engineering and hydraulics.

#### **Alkaline washing**

Data were obtained after washing cans used for transporting sour cream on a modern can washer, equipped with an instrument designed to measure alkalinity in terms of its electrical resistance in order to ensure positive content of the cleaning solution at approximately 0.15 per cent (as Na<sub>2</sub>O) when alkalies were used. In Table III, A and B, the cans were all washed with an alkaline solution; the alkali was compounded to embody the latest improvement in dispersive and emulsifying properties as well as the sulfonated alcohol wetting agents. The particular alkaline product used has enabled many nationally known dairy concerns with extensive research facilities to reduce the variety of cleaning compounds needed for a multiplicity of cleaning operations, at tremendous savings in operation.

In all instances, upon delivery from the can washer, the inside surfaces of the cans were rinsed with 100 ml. of sterile water, and the moistened cans were covered and held 48 hours at



Applying Acid Cleaner Solution as a Spray to a Surface Cooler, Subsequently Cleaned with a Soft Bristle Hand Brush

room temperature. At the end of the 48-hour period the cans were again thoroughly rinsed inside with the same water before it was plated in T-G-E-M agar. All samples were plated in duplicate, and the total counts and proteolytic bacteria counts were computed. One of the duplicate plates was flooded with bromothymol blue indicator for the purpose of counting the acid and alkali formers. The other duplicate plate was flooded with a 0.5 per cent aqueous solution of tetramethyl-p-phenylenediamine hydrochloride, according to the method of Ellingworth, McLeod, and Gordon(3), for the purpose of counting the oxidizing types of bacteria.

We well recall the effectiveness of holding washed cans with the sterile water rinse for the 48-hour period before plating to attest the completeness of the

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Consecutive Can through Washer	Condition of Can	Total Count	Proteolytic Types	Acid Types	Alkali Types	Oxidizing Types	Odor
		А.	Cans Washed with .	Alkali			
300         0           310         0           320         0           330         1           350         1           380         1           380         1           400         1           410         1           430         4           450         4           450         4           490         500           510         510           520         530	Good Good, rusty neck Good, soldered Excellent Good Rusty on bottom and lid Rusty bottom, very poor Good Rust spots on bottom Excellent, new can Excellent, new can Excellent, new can Excellent, new can Excellent, new can Excellent, new can Good Good Good Rust spots on bottom Rust spots on bottom Poor, rust spots on bottom and neck Very poor, rusty Good Good Good Good	$\begin{array}{c} 25,200,000\\ 9,000,000\\ TNTC^a\\ 21,500\\ 48,000\\ 2,090,000\\ TNTC\\ 1,000\\ 4,800,000\\ 4,800,000\\ 4,800,000\\ 1,000\\ 2,000\\ 810,000\\ 1,610,000\\ 1,610,000\\ 1,610,000\\ 1,610,000\\ 1,610,000\\ 1,610,000\\ 1,610,000\\ 1,000\\ 2,000\\ 420,000\\ 1,000\\ 22,000\\ 22,000\\ \end{array}$	$\begin{array}{c} 600,000\\ 800,000\\ 800,000\\ TNTC^{a}\\ b\\ 9,000\\ 30,000\\ TNTC\\ b\\ b\\ 2,000,000\\ TNTC\\ 1,000\\ 2,000\\ 70,000\\ b\\ b\\ b\\ 150,000\\ 1,000\\ 150,000\\ 150,000\\ TNTC\\ 30,000\\ TNTC\\ 9,000\\ 210,000\\ b\\ b\\ b\\ 4,000\\ \end{array}$	$\begin{array}{c} {\rm TNTC}^{a} \\ {\rm TNTC} \\ {\rm 400} \\ {\rm TNTC} \\ {\rm TNTC} \\ {\rm 400} \\ {\rm TNTC} \\ {\rm 400} \\ {\rm TNTC} \\ {\rm 400} \\ {\rm TNTC} \\ {\rm 300} \\ {\rm 600} \\ {\rm TNTC} \\ {\rm 3,500} \\ {\rm TNTC} \\ {\rm TN$	TNTC <sup>a</sup> TNTC TNTC 600 TNTC TNTC 600 1,800 3,000 700 TNTC 700 5,500 TNTC TNTC TNTC TNTC TNTC TNTC TNTC TN	$\begin{array}{c} 4,000\\ {\rm TNTC}^{a}\\ {\rm TNTC}\\ {\rm b}\\ {\rm 800}\\ {\rm TNTC}\\ {\rm b}\\ {\rm 600}\\ {\rm TNTC}\\ {\rm b}\\ {\rm for}\\ {\rm fo$	Very bad Very bad Good clean Fair Fair Fair Bad Bad Bad Bad Bad Bad Bad Bad Bad Bad
DIO	And the second se	B. Alkali-Was	hed and Gluconic-A	cid-Treated Can	9		
$\begin{array}{c} 300\\ 310\\ 320\\ 330\\ 340\\ 350\\ 360\\ 400\\ 410\\ 420\\ 430\\ 440\\ 420\\ 440\\ 450\\ 460\\ 470\\ 480\\ 470\\ 490\\ 500\\ 510\\ 510\\ 520\\ 530\\ 540\end{array}$	Good condition, one soldered spot Poor condition, rust spots Good condition Fair, few rust spots Good condition Fair condition, few bottom spots Good condition Few rust spots on bottom Good condition Good Good Good Very poor, bad bottom Good Rusty lid, otherwise good Good Fair Food Good Fair, few tiny rust spots Fair, few tiny rust spots Good Good, rusty lid	$\begin{array}{c} 2,000\\ 1,500\\ 6,500\\ 1,000\\ 1,000\\ 1,500\\ 14,000\\ 16,000\\ 5,000\\ 85,000\\ 4,000\\ 9,000\\ 14,000\\ 7,500\\ 3,500\\ 3,500\\ 3,500\\ 2,000\\ 13,000\\ 7,000\\ 13,000\\ 7,000\\ 3,000\\ 6,000\\ 28,000\\ 6,000\\ \end{array}$	b b b 2,000 b b b b b b b b b b b b b b b b b b	$\begin{array}{c} 2,000\\ 1,000\\ 3,500\\ 1,000\\ 1,500\\ 12,000\\ 13,000\\ 7,000\\ 5,000\\ 5,000\\ 5,000\\ 5,000\\ 13,000\\ 13,000\\ 13,000\\ 13,000\\ 13,000\\ 13,000\\ 13,000\\ 13,000\\ 3,500\\ 3,500\\ 3,500\\ 3,500\\ 3,500\\ 3,000\\ 5,000\\ 3,000\\ 6,000\\ 6,000\\ \end{array}$	$\begin{array}{c} b\\ 500\\ 3,000\\ b\\ b\\ 3,000\\ 3,000\\ 3,000\\ 4,000\\ 1,000\\ 1,000\\ 1,000\\ 1,000\\ 7,500\\ b\\ b\\ TNTC\\ b\\ b\\ 12,000\\ b\\ b\\ 1,000\\ b\\ b\\ 8,000\\ b\\ b\end{array}$	$\begin{array}{c} 2,000\\ b\\ b\\ b\\ b\\ 5,000\\ 2,000\\ 5,000\\ 2,000\\ 5,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 3,000\\ 4,000\\ 4,000\\ 1,000\\ 3,000\\ 3,000\\ 5,000\\ \end{array}$	Good clean Good clean
		C. Cans W	ashed with Mikro S	an Acid Cleaner			
210 220 230 240 250 300 330 340 450 450 450 450 460 470 500	Good Good Fair, rust spots Fair, rust spots Poor, rusty Good Good Yery poor, rusty Fair, rust spots Fair, rust spots Fair, rust spots Good Good Good Fair, rust spots Poor, rusty Poor, rusty Poor, rusty Good	$1,500 \\ 200 \\ 400 \\ 100 \\ 2,000 \\ 1,600 \\ 12,500 \\ 300 \\ 300 \\ 6,000 \\ 6,000 \\ 6,000 \\ 4,000 \\ 1,000 \\ 11,000 \\ 500 \\ 6,500 \\ 6,500 \\ 10,000 \\ 1,000$	b b b b b d,000 b b b b b b b b b b b b b b b b b b	$1,100\\150\\400\\1,500\\1,500\\1,500\\1,200\\1,200\\300\\5,000\\2,500\\2,500\\2,500\\2,500\\5,900\\5,900\\5,900\\6,000$	$ \begin{array}{r}     400 \\     50 \\     b \\     b \\     500 \\     b \\     500 \\     b \\     b \\     1,000 \\     200 \\     200 \\     2,000 \\     5,100 \\     b \\     500 \end{array} $		Good clean Good clean

 
 Table III. Plate Counts on Tin-Coated Cans Washed by Various Methods and Then Rinsed with 100 Ml. Sterile Water and Held 48 Hours at Room Temperature before Plating on T-G-E-M Agar

cleaning method. For by such a method we demonstrated to one nationally known dairy equipment manufacturer that his very modern can washer could not deliver washed cans that would pass this test successfully with sweet-smelling low-count-bacteria cans, particularly after 50 to 100 cans had been washed. The accumulation of milk solid, etc., in the washing solution itself soon dissipates the dispersive and rinsing properties of any alkali cleaning solution, as discussed in a previous article  $(\delta)$ .

Table III-A gives the comparative data obtained from a series of consecutively alkali-washed cans, subsequently rinsed with hot water (200° F.), steam, and hot air blasts. Attention is called to the relatively high total counts which varied considerably, irrespective of the condition of the can,

although generally speaking, well-tinned cans and particularly some lacquered cans with a Lithcote surface (cans 400 and 430) tended to show better results. Most cans had high proteolytic, acid, alkali, and oxidizing bacteria counts. In spite of the fact that most cans carried high acid-forming bacteria counts, the cans themselves were most objectionable with their proteolytic foul odors.

#### Alkaline wash followed by acidified steam

Table III-B shows the results obtained when a series of consecutively alkali-washed cans were rinsed with steam charged with gluconic acid in sufficient concentration to give a pH 6.0-6.5. There is a definite improvement in all counts as well as in the odor of the cans, although such improvement

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Spraying Sanitary Pipes with Acid Cleaner Solution, Subsequently Cleaned with Motor-Driven Bristle Brush

is not due to germicidal action but to the release of the film of nutrient and bacteria as previously reported (5).

As a matter of fact, this study involving the final rinsing of cleaned milk cans with acidified steam to leave them in a condition of acid reaction suggested the desirability of reviewing critically all equipment and utensil cleaning practice. An alkaline reaction obviously can lead to complications, as already indicated. Then, too, there is no doubt that the more spectacular and more easily controlled oxidation of dairy products and other fatty foods by nonliving catalysts has eclipsed the more complex action of microbiological oxidases. As Jensen and Grettie (4) suggested, food manufacturers and their quality control laboratories could do well to give greater consideration to the oxidative as well as hydrolytic rancidity effects induced by microbial activity in fatty foods.

Relatively little attention has been paid to the oxidizing capacity of microorganisms in relation to the quality impairment of dairy products. We refer not only to the "cappy" flavor of low-count milks but to the surface taints in butter as well as the off-flavors in cheese, all of which have been incidental to the advancement of supersanitation in these industries. Castell and Garrard (1) recently reported that "the spoilage microorganisms involved demonstrate definite oxidizing properties. Organisms of the Pseudomonas and Achromobacter genera are the most strongly oxidizing types; those belonging to Alcaligenes and Brucella are somewhat less, although still strongly positive; members of the Aerobacter, Escherichia, and Proteus are weakly positive, variable or negative; the Bacilli also vary from weakly positive to negative; while the Cocci and the only Anaerobe studied were definitely negative. It is also interesting to note that all organisms which were found to be strong oxidizers were Gram-negative, while those which definitely were not strong oxidizers were Gram-positive."

With sanitarians bending every effort in their programs to eliminate or at least minimize natural types, such as the lactis group normally found in fresh raw milk, and with the growing realization that the strong oxidizers, such as some of the *Achromobacter* and *Pseudomonas* types whose normal habitat is water and soil, have varying resistance to the chlorination of water supplies, we are apprehensive lest supersanitation is engaged in "upsetting the balance of Nature". We are finding that some of the influences in the quality impairment of dairy products are actually being enhanced by the scrupulous efforts for sanitary perfection. While we do not infer a return to "the horse and buggy days", we definitely are of the opinion that more attention must be paid to the final freedom of cleaned equipment from films bearing spoilage types of microbes and nutrients.

#### **Commercial acid cleaner**

Table III-C gives the comparative data from a series of consecutively washed cans subjected to the cleaning action of a commercial acid cleaner known as Mikro San, containing a nontoxic mixture of certain organic acids, specific wetting agents, corrosion-resisting inhibiter, and microbiological depressant. Only 8 ounces of this mixture were used for charging 60 gallons of water in the washing solution compartment of the can washer. After 200 cans were washed, an additional ounce of the mixture was added to the solution for

each additional 100 cans. The cans were cleaned remarkably well and were free from water spots; rubbing the finger over the cleaned surface showed a definite drag which is characteristic of thoroughly cleaned (not polished) metal surfaces. After the 48-hour incubative period, the inner surfaces of the can were dry except for the parts of the bottom holding 100 ml. of rinse water.

Again we note relatively low total bacterial counts, with proteolytic and oxidizing types definitely inhibited; the only two exceptions are in cases of very poor and rusty cansnamely, 340 and 460 which, incidentally, compare favorably with the data reported for similar cans in Table III-A.

The collective data in the tables show the need for further revision not only in dairy can-washing practice but in all types of food sanitation and cleaning practice. Accordingly, the possibilities of acid detergency, have been explored and, as a result, it is soon hoped to develop applications in all types of equipment and utensil cleaning, even including bottle washing. One marked practical effect has been the effectiveness of acid cleaners in solving the thermoduric bacterial count and its attendant water- and milk-stone contamination problems, the bane of every dairyman.

#### Conclusions

Alkaline cleaning compounds have played an important role in many important food sanitation practices. Due to their inherent chemical and physical properties, they have long been recognized as best adapted for such cleaning practices.

Recent experiments, however, have suggested that many of the proteolytic, alkali-forming, and oxidizing types of bacteria are favored in their quality defection of food products when alkaline cleaning is used. Certain conditions of hardness in water supplies utilized as the solvent for many different types of alkaline cleaning compounds have been responsible, at least in part, for the so-called milk- and waterstone deposits on dairy equipment and in cans. This disadvantage presumably does not apply to acid cleaners, for their acid character not only is corrective when used with water supplies predisposed to water-stone formation with

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certain alkaline products but also is curative in that acids will tend to eliminate prevailing calcareous deposits, a practice now generally recognized and widely applied. It is needless to discuss the value of any cleaner that solves the milk-stone problem and its attendant difficulties with thermoduric (heat-enduring) and thermophilic (heat-loving) types of bacteria.

Heretofore acid compounds have been unacceptable mainly because of their inferior detergency as well as their relatively intense corrosive action upon the metals used in food processing equipment. The discovery of organic acids with relatively low corrosiveness gave rise to the development of an acidified steam rinse in the cleaning of milk cans. The attendant inhibiting effects upon proteolytic, alkali-forming. and oxidizing types of bacteria have indicated the desirability of developing acid types of cleaners; generally, more acceptable bacterial flora survive acid cleaning practices in contradistinction to the quality-defective types apparently attendant upon alkaline cleaning. The next logical step was the development of nontoxic, relatively noncorrosive acid cleaners which now are enjoying an ever-widening application in a variety of food industries.

The application of wetting agents and the discovery of their effective combination with acid-reacting substances definitely indicates that the long sought acid cleaning agents, the hope and dream of many a sanitarian, are being realized. Today, therefore, acid cleaning compounds with a detergency even superior to that of most alkaline products, with the lack of any appreciable corrosiveness, and at the same time both corrective to and curative of the problem of water-stone formation and other calcareous deposits, are indicative not only of a revision but of even greater improvement in food sanitary practices.

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#### END OF SYMPOSIUM

# Solidification Point Nomograph for Fatty Acids



**D. S. DAVIS** 

Michigan Alkali Company, Wyandotte, Mich.

N VIEW of the importance of the solidification point of fatty acids as a criterion of purity, Hoerr, Pool, and Ralston<sup>1</sup> presented excellent supplementary data on the effect of water in lowering the freezing points of the normal saturated fatty acids from caproic to stearic, inclusive. Their results may be correlated by the equation,

#### $w/\Delta t = a + bw$

where w is percentage of water,  $\Delta t$  is freezing point depression (°C.), and a and b are characteristics of the fatty acid in question and may depend upon n, the number of carbon atoms.

Data are presented conveniently and reliably  $(\pm 0.02^{\circ} \text{ C})$ in the line coordinate chart based upon the equation and the following constants:

toms	Fatty Acid	a	Ь	Range of w	F. P. of Dry Acid C.
6 7 8 9 10 11 12 13 14 15 16 17 18	Caproic Heptylic Caprylic Nonylic Caprie Undecylic Laurie Tridecylic Myristic Pentadecylic Heptadecylic Stearic	$\begin{array}{c} 0.394\\ 0.383\\ 0.373\\ 0.351\\ 0.370\\ 0.479\\ 0.467\\ 0.574\\ 0.551\\ 0.651\\ 0.743\\ 0.820\\ 0.912 \end{array}$	$\begin{array}{c} 0.289\\ 0.357\\ 0.414\\ 0.476\\ 0.535\\ 0.559\\ 0.678\\ 0.713\\ 0.880\\ 0.924\\ 1.017\\ 1.150\\ 1.183 \end{array}$	$\begin{array}{c} 0.4-2.21\\ 0.4-2.98\\ 0.2-3.88\\ 0.8-3.45\\ 0.9-3.12\\ 0.2-2.72\\ 0.6-2.35\\ 0.2-2.00\\ 0.6-1.70\\ 0.5-1.46\\ 0.4-1.25\\ 0.2-1.06\\ 0.2-0.92\\ \end{array}$	$\begin{array}{c} -3.24 \\ -6.26 \\ 16.30 \\ 12.24 \\ 30.92 \\ 28.13 \\ 43.86 \\ 41.76 \\ 54.01 \\ 52.49 \\ 62.41 \\ 60.94 \\ 69.20 \end{array}$

The use of the chart is illustrated as follows: What is the solidification point of capric acid which contains 3.0 per cent water? Connect the point where n = 10, which represents capric acid, with 3.0 on the w scale and read the lowering of the freezing point as  $1.52^{\circ}$  C. on the  $\Delta t$  scale; then, using the table, the solidification point is 30.92 - 1.52 or  $29.40^{\circ}$  C.

1 Hoerr, C. W., Pool, W. O., and Ralston, A. W., Oil & Soap, 19, 126 (1942).



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HROUGH the courtesy of the Bernheim Distilling Company we are enabled to publish No. 145 in the Berolzheimer series of Alchemical and Historical Reproductions.

This is from a modern painting and shows the famous Italian alchemist, Count Bernardus di Trevisanus (1406–1490), who spent his life from early youth in a search for the philosophers' stone and in trying to make gold from base metal. Like his predecessors and successors he failed, but eventually, on his death-bed, realizing the futility of his "To make endeavors, he whispered: gold one must start with gold."

The artist has, with little and simple apparatus, portrayed the

spirit of the work being done, although it is doubtful that the laboratory was as neat and tidy as shown.

50 East 41st Street New York, N.Y.

D. D. BEROLZHEIMER

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The list of reproductions published during 1941 and 1942 follows. The figures in parentheses following the name of the artist denote the pages on which the respective reproductions will be found. A list of the first 96 reproductions was published in the January, 1939, issue, page 124, and of Nos. 97 to 120 in the January, 1941, issue, page 114.

# 1941

121.	Le Chemiste, Mieris (114)
122.	Chinese Alchemist, Ts'ao (256)
123.	The Alchemist, Webb (374)
124.	Chymischer Goldt Narr, Weigel (549)
125.	Suitland Alchemist, Artist Unknown (581)
126.	Goldmacher Narr, Weigel (786)
127.	De Scheider, Luyken (943)
128.	Two Alchemists, Artist Unknown (1048)
129.	The Alchemist, After Teniers (1153)
130.	Alchymist, Wijck (1330)
131.	Distillation, Stradano (1439)
122	The Concerner Eccention (1500)

#### 1942

- The Studious Alchemist, Artist Unknown (119)
- 134. Hocus Pocus, Rowlandson (216)
  - Porcelain Manufacture, Kiessling (341)
- Distillation, Artist Unknown (448) The Alchemist, Fawcett (602) 136.
- 137.
- 138.
- Spallanzani, Sarra (721) The Alchemist's Explosion, Bentum (838)
- 140. Louis XI at Plessis-les Tours, Ratinckx (942
- 141. Invention of the Devil, Artist Unknown (1118)
- The Apothecary, Artist Unknown (1199) 142.
- 143. Alchemist's Laboratory (1381)
- 144 Chemical Allegory, Moreau (1479)

# SURFACE-ACTIVE AGENTS

#### FOSTER DEE SNELL

Foster D. Snell, Inc., Brooklyn, N. Y.

The oldest surface-active agent is soap, whether made by saponification of fats with alkali or in more complex forms by neutralization of fatty acids with amines. Some of the latter types give a lower pH than that normal to soap or a desired degree of instability on evaporation of the solution.

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Sulfated castor oil is a sulfuric acid ester formed at the hydroxyl groups of glyceryl ricinoleate. Structurally it is a simple step to the sulfuric acid esters of the fatty alcohols, a commercial development made possible by improvements in production methods of these high-molecular-weight alcohols.

Aliphatic sulfonates are represented by esters of sulfosuccinic acid. These are true sulfonates containing  $-SO_2ON$  arather than  $-OSO_2ON$  a. In both sulfated and sulfonated compounds the acid hydrogen is usually neutralized by reaction to give the sodium salt.

Addition of a hydrocarbon side chain and a sodium sulfonate group to an aromatic nucleus forms alkyl aryl sulfonates. This class may rival soap in price when produced in comparable amounts. The nucleus used is predominantly that of benzene, but naphthalene and hydrogenated cyclic compounds also are important.

BY DEFINITION a surface-active agent is one which modifies the properties of the surface layer of one phase in contact with another. In aqueous solution this involves the presence in the same molecule of one or more waterattracting groups and one or more hydrocarbon groups. The broadest definition includes all hydrocarbon derivatives. Depending on the specific properties to be utilized, either the water-attracting or the hydrocarbon groups may predominate, or their effects may be balanced. As an example in which the water-attracting groups predominate, acetic acid is used to promote the wetting of dry solids by water; at the opposite extreme, when oleic acid wets a solid, it becomes more readily wettable by an oil.

The definition of a surface-active agent in common parlance is more limited; it implies a definite degree of balance between the water-attracting and hydrocarbon groups not present in the extreme examples. Thus to produce a properly balanced water-soluble molecule, a long side chain is attached to the ring of sodium benzene sulfonate, shorter ones to sodium naphthalene sulfonate, and none at all to sodium anthracene sulfonate. Without a sufficiently long hydrocarbon group the balance which appears to account for surface activity is lacking. The proportions of water-attracting to water-repelling or hydrocarbon groups may be altered within limits to conform to the purpose for which the agent is to be used. Many terms are used to describe the opposing forces (water-attracting vs. hydrocarbon), such as hydrophylic and hydrophobic, and polar and nonpolar.

Molecular weights of commercial products tend to concentrate strikingly around  $300 \pm 50$ . This suggests that individual water-attracting groups are not powerful enough to balance a longer hydrocarbon chain than corresponds to a molecule of this size. When multiple water-attracting groups

Oleic acid chloride condenses with 2-chloroethylamine and, on subsequent treatment with sodium sulfite, gives Igepon T,  $C_{17}H_{33}CONH(CH_2)_2$ -SO<sub>2</sub>ONa.

Quaternary amines, carrying high-molecularweight hydrocarbon chains, form a reversed type of surface-active agent. Most types such as those already mentioned have an active anion; this has an active cation. Those with an active anion will precipitate with the cation-active type.

Complex ethers and esters with long hydrocarbon chains are nonionizing types of surface-active agents also applicable in nonaqueous media.

The great majority of surface-active agents have —COONa, —OSO<sub>2</sub>ONa, or —SO<sub>2</sub>ONa as the waterattracting group, and a straight-chain hydrocarbon radical of the range  $C_8$  to  $C_{18}$  as the waterrepelling group.

Related manifestations of surface activity are lowering of surface tension, reduction of interfacial tension, increase of wetting power, emulsification, and deflocculation. The rate of development of surface-active agents in the past decade has been great, each new one leading to many more.

are present, as is frequently the case, they must be located at one end of the molecule. If they are a considerable distance apart, the desired orientation of the molecule at the interface is defeated. Compounds which are exceptions to this rule are usually limited as to surface-active properties. For example, the sodium sulfonates of succinic acid esters (2) are relatively high in water-attracting groups, have molecular weights of the order of 350 to 450, and are good wetting agents but deficient in some of the other surface-active properties.

To predict the properties of surface-active agents and so construct compounds with the particular features desired, it would be advantageous if a quantitative expression of the degree of the water-attracting or water-repelling power of a group could be made. This is possible only in a roughly qualitative way. The degree of the water-repelling property of a hydrocarbon group increases with increasing length of carbon chain. Practically speaking, chains of eight carbons and longer are necessary for effectiveness in this direction, although in special cases two somewhat shorter chains may serve in place of a longer one.

Important groups which may be attached to the hydrocarbon chain as the water-attracting unit are, in approximate decreasing order of effectiveness:

-OSO2ONa, -COONa, -SO2ONa, -OSO2OH, -SO2OH

Groups having this effect to a lesser degree are the following:

$$-OH, -SH, -O-, =CO, -CHO, -NO_2, -NH_2, -NHR, -NR_2, -CN, -CNS, -COOH, -COOR, -OPO_3H_2, -OPO_3H_$$

To these must be added unsaturated bonds such as -HC = CH and -C = C which, when present in the hydrocarbon, promote solubility in water; their presence often locates

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OIL WELL PRODUCTION IS IMPROVED BY TREATMENT OF THE OIL-BEARING STRATA WITH ACID CONTAINING SURFACE-ACTIVE AGENTS

water-attracting groups undesirably far apart in the molecule. A strongly water-attracting radical may be substituted by a multiplicity of less powerful groups positioned near each other.

Because of the factor of balance, one cannot compare the effects of two different water-attracting groups attached to the same hydrocarbon chain at the same point and draw reliable conclusions. For example, in measuring the reduction of interfacial tension of an aqueous solution against transformer oil at 60° C. (14), either 0.02 per cent of sodium cetyl sulfate or 0.035 per cent of the corresponding sodium cetane sulfonate is required to reduce the interfacial tension to 10 dynes. Significant differences in the same direction have been found against other media. Results parallel those made by measurement of contact angles in many cases. Yet when lanolin was used as the test medium, the reduction of interfacial tension by equal concentrations of the sulfate and sulfonate in aqueous solution was the same. Lanolin differs from transformer oil particularly in containing water-attracting groups; the balance which was satisfactory in the molecule of the surface-active agent against transformer oil has to be modified at this different interface. These results indicate that sodium cetyl sulfate is in better balance than the corresponding sulfonate when used to lower the interfacial tension at a transformer oil-water boundary. One would predict that with reduction in the length of the hydrocarbon radicals in the two compounds, the effectiveness of the sulfate would drop off before that of the sulfonate; with an increase in length, effectiveness of the sulfonate would drop rapidly.

In contrast, measurement of wetting power by use of the Draves sinking test with a skein of gray cotton yarn shows di-(2-ethyl hexyl) succinate sodium sulfonate to be about ten times as effective as di(2-ethyl hexyl) succinate sodium sulfate (2). Here the balance in the sulfonate is better than in the sulfate which contains a more powerful water-attracting group, too powerful a one.

#### **Properties**

Considering that McBain (7) recently wrote, "It is evident that but little is known of the properties of the surface layers of solutions", a discussion of such properties must be rather generalized. Associated with the study of surface-active agents are experiments dealing with the lowering of surface tension, lowering of interfacial tension, increase in wetting power, deflocculating or dispersing power, deterging effect, foaming action, and, in even less definite terms, cleaning, leveling, and solubilizing power. Few agents possess all of these properties in marked degree; some are more active with respect to certain properties, some with respect to others.

Interfacial tension may be at a solid-liquid, liquid-liquid, or liquidgas boundary, the last having the special name "surface tension". To lower the surface tension effectively when present only in low concentrations, the solute must orient in a suitable concentration at the surface of the solution. When the surface tension is radically lowered, the strength of the surface film is correspondingly lowered and foaming occurs readily. Possibly this is the simplest property to visualize because orientation of the solute

molecules at only one surface is involved and sorption at an adjacent surface cannot take place. Any water-soluble surface-active agent lowers surface tension to some degree although not necessarily enough to cause foaming.

At a liquid-liquid boundary, orientation of the solute molecule, with the water-attracting end in the aqueous medium and the hydrocarbon end in the other, closely parallels the orientation at a gas boundary where the hydrocarbon end is toward the gas. When the interface is solid-liquid, sorption of the solute on the surface of the solid probably occurs. A needle can be made to float on the surface of plain water, but when a little soap solution is added, it will sink. This simple example is an easily observable illustration of the lowering of interfacial tension at a solid-liquid interface.

In all three cases of lowering interfacial tension, an appreciable time is often required for the molecules to become oriented in a way to give the maximum effect. If the waterattracting properties predominate over those of the hydrocarbon chain, a modification to a longer hydrocarbon chain would be expected to promote lowering of interfacial tension, up to a point where solubility is too radically reduced. Reduction in the aqueous solubility of the product is also brought about by addition of salt. These same modifications promote formation of colloidal micelles so that effects due to change in solubility and to micelle formation blend into each other. To illustrate this dual effect, addition of salts decreases the solubility of sodium cetyl sulfonate and simultaneously increases the power to lower interfacial tension. These same salts promote micelle formation. The effects of salts on solutions of Igepon T is even more marked (12). This conforms in degree to the Schultz-Hardy rule for coagulation of colloids by oppositely charged ions where trivalent ions are several times as effective as bivalent ions, which are correspondingly several times as effective as monovalent. Thus a 0.005 per cent solution of Igepon T shows an interfacial tension of 11  $\gamma$  against transformer oil; addition of sodium chloride to make the solution 0.25 N reduces this to 3.5  $\gamma$  (the value is 0.8  $\gamma$  in 0.0025 N calcium chloride solution and 0.25  $\gamma$  in 0.0001 N lanthanum chloride solution). This suggests a relation between conventional colloid formation, micelle formation, and interfacial tension. Too much weight must not be given to interfacial tension reduction alone as a measure of detergent power because other factors are also important.
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The term "wetting power" is variously used as meaning the process of wetting, the degree of wetting, the ease of wetting, or the speed of wetting. In many applications speed of wetting is important, and a distinction is made between immediate and ultimate wetting power. When liquid wets liquid, efficiency of wetting increases with the approach to an angle of contact of  $0^{\circ}$ . This also applies to a liquid and a plane solid. As applied to powders, Bartell defines wetting power in terms of his cell as the energy expended to bring a liquid into contact with the powdered solid.

When a surface-active agent promotes wetting of one liquid by a second, its molecules at the interface orient themselves with the water-attracting groups in water and the hydrocarbon group in the nonaqueous liquid, analogous to orientation in surface tension reduction. It follows that hydrocarbons must be soluble in the liquid being wet by the aqueous solu-When a surface-active agent promotes wetting of a tion. solid by water, the hydrocarbon groups of the agent are sorbed and leave the water-attracting groups facing the aqueous phase. An industrial application of wetting is in the froth flotation of minerals. The valuable mineral is preferentially wet by a collector such as oleic acid or various oils. In operation air bubbles displace the solution at the surface of the mineral, and it collects with the attendant foam at the surface. The air bubbles do not displace the solution from the more completely wet gangue which, therefore, does not go into the foam layer. When the collector is a xanthate, ROC(=S)SNa with R from C2 to C5, reaction may occur with the mineral instead of sorption to produce the necessary waterrepellent surface on the mineral.

In a specific example illustrative of the effectiveness of a wetting agent (9), plain water sprayed on a vertical lacquered surface was retained in an amount of 200 mg. per square inch, but when the water contained a surface-active agent which made no appreciable change in viscosity, an additional 20 mg. per square inch was retained.

Emulsifying power is a measure of the effectiveness of the agent concentrated at the interface in preventing dispersed droplets of an immiscible liquid from coalescing, or in some cases, of its effectiveness in producing spontaneous emulsification. It measures the ability of the surface-active agent to serve as a key or link between the dispersed phase, usually oil, and the dispersion medium, usually water. Intramolecular balance so that the emulsifying agent will concentrate in the interface is essential. Orientation of hydrocarbon and water-attracting groups is also a factor. While the majority of emulsions are oil in water, the reverse, water in oil, is not rare. Alkali soaps promote emulsions of oil in water, waterinsoluble soaps those of water in oil. Reasoning by analogy, a branched-chain hydrocarbon radical should be more effective for water in oil than a straight chain. Many of the agents balanced to serve effectively as wetting agents do not serve as emulsifying agents. No case comes to mind, however, of an effective emulsifying agent which is not at least a fair wetting agent.

Deflocculating or dispersing power is a measure of the efficiency with which agglomerates of solid particles are broken up and suspended in a liquid. The agglomerates or flocculates are not to be visualized as having solid-solid interfaces but as a loosely packed skeleton of particles wet by the liquid on all sides. Residual forces still act to hold one particle in contact with another while friction prevents closer packing. Flocculation may be manifested by thixotropy or false body of paints or inks.

Deflocculation consists of separating the particles so that residual forces no longer act between them. This can be made permanent by sorption of the agent on the surface. Deflocculation causes a paste to assume more nearly the properties of a liquid. Many deflocculating agents are not among those usually considered surface active. Blown or oxidized oils in the paint industry often serve as deflocculators and therefore are in a sense surface active. It should be mentioned that deflocculation in a paint is not always desirable. If there is no flocculation, settling of the pigment may occur to produce close packing; with the desired limited degree of flocculation this does not occur.

The term "detergency" is broadly used with respect to surface-active properties. Actually it has many meanings, depending on whether the surface being deterged is silk, wool, cotton, lacquer, oxidized oil, or metal; on whether the soil being removed consists of solid particles, oiled solid particles, or oil; and on the nature of the oil when present. Oil usually forms a film on soil so that the problems are generally those of an oil-water interface. Steps in detergency which precede and have no direct relation to surface activity may be necessary—for example, neutralization of acidity of the soil. In

the removal of oiled soil from surfaces, the major surface-active factors are ability of the detergent solution to wet both of the surfaces concerned, and emulsifying power. The fine particles of soil are believed to be dispersed by the surfaceactive agent with their oil films intact, so that removal of the soil by dispersion really consists of emulsification.

In a study of the removal of oil from wool by sodium alkyl sulfate solutions (13), the detergent solution preferentially wets the wool fibers, displacing the oil as droplets up to 50 microns in diameter. The initial stage of the formation of such droplets adhering to the wool is followed by their detachment by slight mechanical action. Thus the contact angle has been altered from 180° to 0°. The surfaces of the droplets and of the fibers are probably saturated by the adsorption of molecules of the surface-active agent. These observations would seem to negate the view sometimes advanced that removal of oil takes place by its solution in the micelles of the active agent.

Courtesy, Cuban-American Manganese Corporation IN FROTH FLOTATION OPERATIONS, THE MINERAL IS SEPARATED FROM THE GANGUE BY DIFFERENTIAL WETTING WITH A SURFACE-ACTIVE AGENT; SHOWN HERE IS A SECTION OF FLOTATION CELLS



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### Soaps

No doubt the first surface-active agent was prepared by mixing wood ashes with rancid or scorched fat some time prior to the invention of writing. Soap is still the most important of these agents. To permit comparison of its composition with that of other surface-active agents, Table I shows the complete structures of sodium stearate and sodium oleate. The relatively large size of the hydrocarbon group as compared with the water-attracting group is thus visualized.

All salts of organic acids of an 8-carbon chain or longer are soaps; if the metallic ion is an alkali, they are water soluble. It is possible that some surface-active properties of one type or another can be detected with sodium or potassium salts below Cs, but if so, they are not well known. The C10 soaps are the first to show definite evidence of colloidal behavior. The sodium soaps of lauric, C12, and myristic, C14, acids show greater colloidal properties and greater wetting power. Above that level solubility in cold water decreases. Sodium stearate, C18, is substantially insoluble in cold water and therefore ineffective as regards surface-active properties in cold

water. Introduction of a double bond increases solubility in cold or tepid water. In practice sodium stearate is used in hot water (60° C. or over) and sodium oleate in warm water (30° C. or over). Under such conditions the surface activity as manifested in detergency is good. At low temperatures lathering is at a maximum with a carbon chain of  $C_{12}$  or  $C_{14}$ , but the stearate lathers well in water hot enough to dissolve it.

Balance is satisfactory in soaps containing saturated hydrocarbon chains of about  $C_{12}$  to  $C_{18}$ . But that this can be thrown off rather easily is shown by special soaps. Poorer as detergents are soaps of linoleic acid (a  $C_{18}$  acid with two double bonds), of linolenic acid (a  $C_{18}$  acid with three double bonds), and of ricinoleic acid (a  $C_{18}$  acid with a double bond and a hydroxyl group). In each case the additional waterattracting group or groups is not so located as to give proper orientation. These soaps are good wetting agents but less efficient detergents, which would indicate that they lack the proper structure to give good deflocculation or good emulsification.

Although they are the basis of the soap industry, the alkali salts of fatty acids represent a mere beginning of the soap type of surface-active agents. As an illustration three ethanolamine soaps may be formed:

$CH_3(CH_2)_7CH = CH(CH_2)_7COONH_3CH_2CH_2OH,$	amine oleate
$CH_{3}(CH_{2})_{7}CH = CH(CH_{2})_{7}COONH_{2}(CH_{2}CH_{2}OH)_{3}$	diethanol- amine oleate
$CH_{3}(CH_{2})_{7}CH \longrightarrow CH(CH_{2})_{7}COONH(CH_{2}CH_{2}OH)_{3},$	triethanol- amine oleate

Other soaps are obtainable with a whole series of amines derived from the nitroparaffins, from morpholine, and from ammonia itself. Each change in the cation produces changes in the properties of the soap—modifies the balance.

Some of the amine soaps are effective at lower pH levels than the alkali metal soaps, but nearly all are unstable during evaporation of the solvent. In some applications this insta-



Courtesy, Freeport Sulphur Company

SOAP OR OTHER SURFACE-ACTIVE AGENT IS ADDED TO INSECTICIDES TO PROMOTE WETTING OF THE FOLIAGE AND THEREFORE BETTER RETENTION OF THE INSECTICIDE

Detergency is not completed until the soil has been suspended in the detergent solution with sufficient stability so that it can be rinsed away rather than redeposited. Stable dispersion of the soil is usually the controlling factor in detergency. Sorption of the surface-active agent at the interface may produce this stable suspension although some evidence indicates that micelles of like charge function to stabilize the suspension of soil. Thus the addition of a minute amount of colloidal material to a detergent often gives a disproportionate improvement in detergency.

In some cases a limited amount of mechanical action aids detergency, while more gives poorer results. A more common case of poor practice is that of a badly soiled fabric being washed in the same bath as a relatively clean one, when soil from the former may be deposited on the latter. In both cases the factor of danger is the instability of the emulsion of oiled soil. Some substantiation of this is furnished by the observation of Donnan that the lower limiting length of the carbon chain in soaps to give good detergency is the same as the limiting length of the chain to give good emulsification (3).

To summarize, all agents that have surface-active properties lower interfacial tension, including many not usually thought of as surface active. Given sufficient time for orientation at the interface, these would improve wetting, although possibly to a small degree only. Unless the balance in the molecule is good, the compounds may not have definite emulsifying properties or may not be sorbed at the solidliquid interface in sufficient quantity to prevent flocculation. Detergency is not a single phenomenon but a combination, usually dominated by deflocculating or emulsifying power according to whether the soil is free from oil or is oiled.

It is never safe to assume that surface-active agents are interchangeable, or can be replaced and juggled at will. Replacement of soap with saponin in sulfur suspensions reduces their effectiveness (4) for use as insecticides and fungicides. Substitution of sodium alkyl sulfates for sulfated oil has for some purposes proved unsatisfactory. Many surface-active compounds are salts, and their character as electrolytes must be taken into account.

### TABLE I. STRUCTURAL FORMULAS

C17H35- COONa Sodium tearate)	C <sub>17</sub> H <sub>33</sub> COONa (Sodium Oleate)	C18H36O- SO2ONa (Sodium Oleyl Sulfate)	Sodium Ricinoleyl Sulfate	Dihexyl Sodium Sulfosuccinate	Igepon T	Twitchell Reagent	Sodium Keryl Benzene Sulfonate	Trimethyl Cetyl Ammonium Chloride
CH₃	CH3	CH3	CH₃	$CH_3$	CH₃	$\operatorname{CH}_{1}{}_{3}$	CH3	CH3
CH:	CH2	CH2	CH2	$CH_2$	CH2	CH2	CH2	ĊH2
CH:	CH1	CH2	CH2	CH <sub>2</sub>	CH2	CH2	CH3	CH2
CH1	CH2	CH2	CH2	$CH_2$	CH2	CH2	CH2	CH.
CH2	CH2	CH2	CH2	CH <sub>2</sub>	CH2	CH2	CH2	CH2
CH2	CH,	CH2	CH2	CH2	CH2	CH2	$\operatorname{CH}_2$	$CH_2$
CH3	CH2	CH2			CH2	CH <sub>2</sub>	CH3	$\operatorname{CH}_2$
CH2	$CH_2$	CH2	HC-0-S-	-ONa I C==0	$CH_2$	CH2	Ċ <b>H</b> ₂	CH2
CH2	CH	CH	CH <sub>2</sub>		CH	CH2	CH2	ĊH2
CH2	CH	CH	CH		CH	$CH_2$	CH2	ĊH2
CH2	CH2	CH2	CH	CH <sub>2</sub>	CH2	CH2	CH2	CH2
CH:	CH2	CH3	CH <sub>2</sub>	C=0	CH2	CH2	$CH_2$	CH2
CH2	CH2	CH2	CH2	Ŏ	CH2	CH <sub>2</sub>	$CH_2$	CH2
CH,	CH2	CH2	CH2	CH <sub>2</sub>	$CH_2$	CH2	CH2	CH2
CH2	CH2	$CH_2$	CH2	CH2	CH2	ČH2	CH2	CH2
CH2	CH2	CH2	CH2	CH2	CH2	CH2	CH2	CH2
CH2	CH2	CH2	CH2	CH2	CH2		ĊĦ	CH3
C==0	C==0	CH2	CH <sub>2</sub>	CH2	c=0		СНСН	H <sub>3</sub> C—N
 ONa	ONa	0	C==0	CH3	H—N	C=0 SO <sub>3</sub> H	сн сн	CI CH
		0-S-0	0		CH2	0 H	Č	
		ONa	$H_2C$ —R		CH2		0=s=0	
					0=5=0		ÓNa	
					ONa			

bility is a virtue, for surface-active properties are thereby destroyed. An example is the use of such soaps in water-dispersion self-polishing waxes, where they serve as emulsifying agent for the wax and as wetting agent during application. Later the soaps break down by evaporation of ammonia, leaving a wax film that is substantially waterproof. Sometimes included in the soap classification are the naphthenic acid soaps, alginic acid soaps, and others, some of rather limited surface-active properties.

Soap has definite limitations. All practical concentrations of the alkali soaps have a neutral point at about pH 10.2. They can be used at higher pH values but begin to decompose below that level. An exceptional use at lower pH values is oleic acid half neutralized with potassium hydroxide or an amine, so that it is an acid soap soluble or dispersible in organic solvents such as dry cleaners' naphtha. A small amount of water associated with such soaps probably participates in their performance as detergents.

In aqueous solution soaps react with heavy-metal or alkaline-earth ions to give insoluble precipitates. Therefore the second drastic limitation on soaps is that in hard water sufficient soap must be added to precipitate the hardness before a further amount of soap can be effective as a detergent. This defect is partially overcome by addition of a complex phosphate such as hexametaphosphate, tetrapyrophosphate, "tetraphosphate", or tripolyphosphate. This does not affect the pH limitation.

The variety of soaps of various cations with varying lengths of fatty acid chains provides every surface-active property desired. It is a fair statement that, except for the two limitations noted, soaps meet nearly all requirements. Only because of these limitations have the classes of synthetics which follow, been developed. Essentially each is an effort to muzzle or replace the carboxyl group so that alkaline earth compounds are not precipitated, and to provide a product which is stable below pH 10.2.

### **Sulfated Aliphatic Esters**

Historically the second surface-active agent developed was probably that resulting by treatment of castor oil with sulfuric acid. Esterification of the hydroxyl groups of the ricinoleic acid glyceride takes place by reaction with concentrated sulfuric acid.

In this connection a sharp distinction must be made between sulfated and sulfonated products. The former are

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esters of sulfuric acid with an alcohol; the latter are compounds in which a direct carbon-sulfur linkage has been produced, as shown by the formulas  $R_{--}O_{--}SO_2_{--}OH$  and  $R_{--}SO_2_{--}OH$ . Confusion is not lessened by the fact that commercially the sulfates of castor oil are known as sulfonated oils, a misnomer recognized in the trade. Frequently production and names of other sulfate compounds are designated incorrectly "sulfonation" and "sulfonates" rather than "sulfation" and "sulfates".

Sulfated castor oil became important as a wetting-out agent in neutral or acid solution in dyeing, under the name of Turkey-red oil. It is relatively stable in the presence of the low concentrations of calcium and magnesium compounds found in hard water. One defect of sulfated castor oil is that sulfation is never complete so that the same grade differs from batch to batch, and uniformity is only approximated by the blending of several batches. Another is that, while in some degrees of sulfation it is a good wetting agent, its power to lower interfacial tension is rarely adequate to make it of value for deflocculating and emulsifying.

One third of the molecule of sulfated glyceryl triricinoleate is shown in Table I, where R represents two further carbons of glycerol with their accompanying esters. By visual comparison of the formulas, the molecule is seen to be about three times as large as that of soap. This suggests one possible reason for the limitations of its surface-active properties namely, a molecular weight range of 900 to over 1000 with a complexity of water-attracting groups in various parts of the molecule. Under conditions of perfect sulfation, these would include three sulfuric and three carboxylic esters.

The most that can be said for sulfated castor oil is that it furnishes a surface-active agent which is inferior to soap but which has some effectiveness under conditions where soap is unstable. Several other fats and oils are sulfated, but their compositions are so indefinite and their uses so limited as not to merit discussion.

### **Aliphatic Sulfates**

The reaction to form a sulfuric ester at a hydroxyl group may be applied to any alcohol. When long-chain alcohols became available in quantity by the catalytic reduction of fatty acids, a whole group of compounds in this class became commercial. The reaction is direct esterification with sulfuric acid followed by neutralization. The fatty chain varies in length from C<sub>8</sub> to C<sub>18</sub>, the same range as soap, and may be straight or branched as in RCH<sub>2</sub>OSO<sub>2</sub>ONa or R(R')CHOSO<sub>2</sub>-ONa. The alcohols produced by the catalytic reduction of fatty acids are usually oleyl, stearyl, mixed alcohols from the fatty acids derived from coconut oil, or purified fractions of these alcohols consisting mainly of lauryl or myricyl alcohol. Branched-chain alcohols for this purpose are purely synthetic.

The structure is closely related to that of soap; the waterattracting group—COONa has been replaced by —OSO<sub>2</sub>ONa, and the lengthening of the hydrocarbon chain by one —CH<sub>2</sub> has been purely incidental. Comparison of the structures of sodium oleate and sodium oleyl sulfate in Table I illustrates this. One might even simplify this comparison by saying

that the -C in the water-attracting group has been reo placed by -O. Unlike soaps, alkyl sulfates are stable

in neutral solutions. Even when in distinctly acid solution the free acid is sufficiently water attracting as to have surfaceactive properties; for example, such solutions still foam.

Courtesy, Freeport Sulphur Company DIPPING GOATS IN WETTABLE SULFUR SOLUTION FOR THE CONTROL OF LICE

The sulfated alcohols are relatively stable to hard water. This permits their use as a "soap" in hard water areas. They do not hydrolyze in water. As an illustration of the result of this (10), the residual oil in lightly oiled wool is increased rather than decreased when the wool is deterged in soap solutions below 0.05 per cent. This increase is due to sorption of fatty acid from hydrolysis. No parallel phenomenon is found when sodium alkyl sulfates are used or if the wool is previously saturated with aqueous alkali.

The surface-active properties of the sulfated alcohols vary with the length of chain, wetting power increasing from  $C_{12}$  to  $C_{18}$ . They may be given such a variety of balance of waterattracting and hydrocarbon groups as to embrace nearly as wide a range as that of soaps. They represent a solution to both of the two serious limitations of soap. Their only real handicap is cost. The alcohols must be produced from fatty acids, which in turn come from fats, so that more steps are necessary in production than with soap. Therefore one can predict with reasonable assurance that the cost on a basis of an equal content of active agent cannot be so low as that of soap. Commercially, grades from different manufacturers contain from a few per cent to over 50 per cent of sodium sulfate, a confusing factor in making comparisons by weight of product.

If the sodium salts of both a sulfuric acid ester group and a carboxyl group are attached to a  $C_{18}$  molecule, the balance shown by a soap or a sulfated alcohol would be expected to be thrown off. This is true of the sodium salt of sulfated ricinoleic acid, an even poorer detergent than the plain or unsulfated soap of that acid, which is unsatisfactory commercially.

As with soap, practically any alkaline agent may be used to neutralize the alkyl sulfuric acid, the triethanolamine salt having been marketed as a commercial shampoo. This had only one defect—it was so efficient as a detergent that it removed not only the soil from the hair but so much of the natural oil that the product had to be "improved" in practical terms by making it less efficient as a detergent.



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### **Amide Derivatives**

Conversion of the carboxyl group of a fatty acid to an amide produces the fatty amides. They are substantially insoluble in water. After the carboxyl group has been rendered inactive, it is necessary to introduce more water-attracting groups if the material is to be surface active in aqueous solution. A suitable method is by adding an ethylene sulfonic acid group to the amide; one technique is by the reaction of oleyl chloride with the sodium salt of taurine to give Igepon T ( $\delta$ ). The structure is shown in Table I; the water-attracting group introduced is a sodium sulfonate rather than a sodium sulfate. The structure closely resembles those of sodium oleate and sodium oleyl sulfate except that it has two more carbons, which are probably offset by the modest waterattracting property of the substituted amide group.

This is a well balanced surface-active compound effective in wetting, emulsifying, deflocculating, and foaming action. It gives good detergency, is stable in both acid and alkaline solutions, and is not precipitated by calcium and magnesium. The corresponding sulfate can be made by reaction of the amide with ethylene oxide to give the alcohol, followed by sulfation. Such a procedure, therefore, is a second method of overcoming the two inherent defects of soap.

### **Aliphatic Sulfonates**

Having a sulfated alcohol, such as sodium oleyl sulfate, and a sulfonated chain, such as Igepon T, it might seem logical to produce sodium oleyl sulfonate. This can be done indirectly but is not a commercial process. The solubility of the calcium and magnesium salts has been found to be low (11), usually even less than the published values for calcium and magnesium soaps. They cannot take the place of the corresponding sulfates in overcoming the effect of hard water.

Minor amounts of sulfonates are present in sulfated castor oil if the temperature is allowed to rise during sulfation. Some are produced by sulfonation of unsaturated petroleum



Courtesy, Colgate-Palmolive-Peet Company

SOAP KETTLE, SOURCE OF THE MOST WIDELY USED SURFACE-ACTIVE AGENT, INTO WHICH A QUARTER MILLION POUNDS OF RAW MATERIAL CAN BE CHARGED AT ONE TIME

fractions, the reaction at an aliphatic double bond being an addition:

$$\begin{array}{c} H_{\rm C}^{\rm I} \\ H_{\rm C}^{\rm I} \\ H_{\rm C}^{\rm I} \end{array} + H_2 {\rm SO}_4 \longrightarrow \begin{array}{c} H_{\rm C}^{\rm I} - {\rm SO}_2 {\rm OH} \\ H_{\rm C}^{\rm I} - {\rm OH} \\ H_{\rm C}^{\rm I} - {\rm OH} \end{array}$$

Such petroleum sulfonates may be predominately aromatic or aliphatic, according to the source of the raw material—i. e., from naphthenic or paraffinic crude. These petroleum sulfonates are recovered from the sulfuric acid refining of oil as mahogany sulfonates which may be further purified, or they are produced by sulfonation of fractions obtained by sulfur dioxide extraction. Sulfite extract, a by-product from spruce pulp, contains lignosulfonic acids. A synthetic ester type of sulfonate somewhat similar to Igepon T has the formula  $CH_3(CH_2)_7CH=CH(CH_2)_7COO(CH_2)_2SO_2ONa$ . All of these are of relatively minor importance although some are commercial products.

Complex products in which the ester appears to be more stable result from addition of sodium bisulfite to the double bond of a succinic acid ester. These have been extensively studied and commercialized primarily as wetting agents (2, 15). A typical structure, that of the dihexyl ester, is shown in Table I. The usual long-chain hydrocarbon group is replaced by two shorter hydrocarbon radicals.

These compounds furnish excellent examples of the variation in solubility and surface-active properties with alteration of balance between the water-attracting and hydrocarbon groups. The typical structure is:

$$NaOSO_2$$
—CHCOR

If R is a  $C_{12}$  chain, the material is substantially insoluble and therefore ineffective as a surface-active agent in water. What its properties may be in other solvents is unknown. As the

size of the two hydrocarbon groups is reduced, the solubility in water would be expected to increase, and does to give the following solubilities at 30° C.: C10 0.15 per cent, C<sub>9</sub> 0.47, C<sub>8</sub> 0.7, C<sub>7</sub> 3.3, C<sub>6</sub> 13.5, C<sub>5</sub> 23, C<sub>4</sub> 32. If an aqueous solution of the C<sub>4</sub> ester is reduced to a concentration of 1 per cent, it shows no effective wetting power. Yet the C4, C5, C6, and C8 compounds are all commerical products. The effectiveness of the C<sub>8</sub> compound is radically reduced as salt is added, and at sufficient electrolyte concentrations it can be salted out. On the contrary, the effectiveness of the C4 ester improves with electrolyte addition so that in 20 per cent sodium sulfate solution it is nearly as effective as the C<sub>6</sub> ester in water. Studies of many mixed esters (2) lead to the generalization that solubility decreases and wetting power increases with an increasing length of the hydrocarbon radical up to 16 carbon atoms. As a general rule, esters of secondary alcohols in this series are more soluble in water than those of primary alcohols.

The behavior of the  $C_4$  ester in salt solution suggests that, when solubility is reduced to an adequate degree, micelle formation starts and surface-active properties are improved. Since, as previously mentioned, the same conditions promote sorption, that could also be the factor involved.

Under somewhat parallel conditions (18), a 0.03 per cent solution of Igepon T at 35° C. did not lather or deterge soiled wool at pH 1 or 3, but the addition of 5 per cent salt caused it to foam and give good detergency. The increased solubility of the amine in acid solution was overcome by the addition of salt, just as the inherently excessive solubility because of the short hydrocarbon groups was overcome with the C<sub>4</sub> ester.

### **Alkyl Aryl Sulfonates**

Benzene sulfonic acid shows some surface-active properties, toluene sulfonic acid more. Practically a longer side chain than the methyl radical is desirable to produce an adequate hydrocarbon character. Given the essentials of an aromatic nucleus with a sulfonic acid group as the sodium salt attached and an aliphatic side chain, one has a structure related to soap by a series of easy transitions.

The simplest form is a benzene derivative such as keryl benzene sulfonate, keryl meaning an aliphatic radical of the order of magnitude of that of the kerosene fraction. Naphthalene as a fused double radical is also used, as are diphenyl, phenylphenol, and anthracene. These aromatic radicals may be hydrogenated and alkylated. A typical structure is shown in Table I; this length of side chain, which is near the upper limit of the range for the keryl group, is selected because it is most closely analogous to the other compounds shown. It differs from Igepon T only in having the C<sub>6</sub>H<sub>4</sub> radical to bridge from the hydrocarbon to the sulfonic acid salt instead of the group —CONHCH<sub>2</sub>CH<sub>2</sub>—. Another example of this type (Table I) is the fat-splitting reagent of Twitchell, the product of reaction of oleic acid, naphthalene, surface-active agents in terms of the amount of active agent present, but raw materials are practically unlimited and costs may well be expected to fall to the same order of magnitude as that of soaps.

### **Esters and Ethers**

The carboxyl groups of a fatty acid can be muzzled by conversion to an ester, but the limited solubility of an ester such as ethyl oleate renders it almost useless. This condition would be improved if additional water-attracting groups were introduced. Thus it seems reasonable to make the monoesters of fatty acid with ethylene glycol and glycerol, thus adding either one or two hydroxyl groups, respectively. Such products have a market although they are often not designated as surface-active agents.

An interesting reaction for production of the glycol ester is direct addition of ethylene oxide to oleic acid:

 $C_{17}H_{33}COOH + (CH_2)_2O \longrightarrow C_{17}H_{33}COO(CH_2)_2OH$ 

The corresponding reaction with a fatty alcohol gives an ether:

$$C_{17}H_{33}OH + (CH_2)_2O \longrightarrow C_{17}H_{33}O(CH_2)_2OH$$

Even polymerization of ethylene oxide alone will build up a sufficiently large molecule to have surface-active properties, probably due to micelle formation as the structure does not conform to conventional requirements for orientation at an interface. One example of such a structure has approximately the composition  $HOCH_2(CH_2OCH_2)_{90}CH_2OH$ .



COMMERCIAL LAUNDRIES ARE IMPORTANT USERS OF ALL TYPES OF SURFACE-ACTIVE AGENTS

and sulfuric acid or  $2(\beta$ -sulfonaphthyl) stearic acid. The reagent must produce intimate wetting of fat by water if reaction is to take place. Some other wetting agents can be used in place of this one.

The alkyl aryl sulfonates are suitable for use in hard water and possess one outstanding advantage, that of low price in the usual commercial grade, which contains about 65 per cent of sodium sulfate. Not only are they the lowest priced All classes of surface-active agents considered up to this point have been anion active. In the ethers and esters there is in no case a strongly water-attracting group. Rather that property is supplied by more than one group, usually several. Such groups differ from any previously discussed in that no ionization occurs. They are usually better as wetting agents than in other surface-active properties. Thus if in Table I the Na of sodium stearate is replaced by  $-CH_{T}$ -CHOH- 10

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CH<sub>2</sub>OH, the result is glycerol monostearate, a typical nonionizing surface-active ester.

### **Cation-Active** Compounds

Another class of surface-active compounds, sometimes referred to as reversed soaps or invert soaps, are so constructed that the major part of the molecule is positively charged. While the patent literature shows a large number of possibilities such as betaine derivatives, phosphonium compounds, etc., practically speaking, the commercial compounds are quaternary ammonium derivatives.

As in the other types, the long-chain hydrocarbon radical is essential. Table I shows the structure of the simplest member, trimethyl cetyl ammonium chloride. The inert character of the hydrocarbon residue is demonstrated strikingly by the reversal of charge of the ion composed mainly of the hydrocarbon radical by replacement of -COONa or  $-SO_2ONa$  by  $-N(CH_3)_3Cl$ . The following illustrate structures which prove to be effective cation-active agents:



cetyl pyrydinium chloride

The halide is replaceable by other radicals of strong acids,  $-HSO_4^-$  for example. In each case the product ionizes with the halide or equivalent as negative ion and the rest as positive ion. In addition to the water-attracting nature of the quaternary ammonium halide  $\equiv N-X$ , in many cases additional solubility is introduced with substituents such as the pyridinium radical.

The cation-active compounds are designed primarily for use in acid or neutral solution, where they possess effective foaming, deflocculating, and emulsifying properties. Broadly speaking, they may be visualized as the equivalent detergent in acid solution, to a soap in alkaline solution. Being of like charge, the surface-active ion cannot react with heavy-metal ions.

### **Agents for Nonaqueous Media**

A water-attracting group in a surface-active compound serves to solubilize a large hydrocarbon radical in water. The reverse is seldom true so that the classes which are sodium salts of strongly water-attracting groups will not usually dissolve in nonaqueous media. Because of the mildness of its water-attracting groups, the nonionizing type is the class ordinarily used in nonaqueous media. In some cases the cation-active type will dissolve and is effective. But the majority of the agents used in nonaqueous media are used for their surface-active properties without a clear recognition of those properties, and are not synthesized for the purpose. Thus in the frying of doughnuts in fresh grease, browning of the outer surface may not take place even when the doughnut is well cooked. Building up of a fatty acid concentration in the grease adequate to promote wetting will correct this. With too much fatty acid, the doughnuts brown before they are cooked.

#### Extenders

Many, although not all, of the commercial surface-active agents are extended with material which is not surface active. The usual grades of sodium alkyl sulfates are typical. They are in general produced by sulfation of the alcohol with excess of sulfuric acid. In order to obtain the sodium salt, it is customary to neutralize, often with sodium carbonate, and thus produce sodium alkyl sulfate plus sodium sulfate from the excess of sulfuric acid. It is not unusual to find from one half to two thirds of commercial surface-active preparations consisting of extender, usually sodium sulfate.

But however simple it may seem to classify the surfaceactive agent as active material and the salt as inert, this may or may not be correct. If the balance of the surface-active agent is correct for the particular conditions of use, addition of a salt may render it less effective. If the surface-active agent is somewhat more soluble than it should be, the salt may correct this by promotion of micelle formation or sorption or both. Similar to the building of soap solutions with alkaline or neutral salts in suitable proportions, in deoiling wool yarn, a close parallel is found (10) between the effectiveness of sodium chloride, sodium sulfate, sodium hexametaphosphate, and tetrasodium pyrophosphate in "building" sodium alkyl sulfate. Other examples of salt effect have been discussed under aliphatic sulfonates.

### **Typical Uses**

Unquestionably the properties of surface-active agents were utilized long before their fundamental character was appreciated. Even today many applications are made by rule of thumb based on practical experience rather than on theoretical considerations.

In the textile field one usually thinks of the aim in wetting fabric as that of promoting the ease of sorption and uniformity of take-up of a dyestuff. Yet for level dyeing this controlled degree of sorption is desirable; it is often not the maximum because too rapid sorption may be uneven. The rate of sorption can be controlled by adding a wetting agent of like-charged ion. Thus an anion-active agent added to a bath containing acid dye, since each gives a large negatively charged ion, slows down the sorption according to the amount of agent added. A cation-active agent serves similarly with a basic dye.

A cation-active and an anion-active agent react to form a precipitate or an oil. Therefore if a cotton fabric, which is negative, is treated so that it strongly sorbs a cation-active agent, it will have the properties of animal fabric, which is positive at low pH levels. The treated cotton will then dye like wool and not like cotton. An anion-active agent will have the reverse effect on wool or silk.

One of the more striking illustrations of surface activity or, more specifically, of wetting power is negative, that of waterproofing. If a textile fabric is treated with aluminum stearate or any of a large number of other agents to lessen the ease of wetting by water, the contact angles become such that the water cannot enter the pores of the fabric. The net result is that with ample openings the fabric still repels water. Commercially, cation-active agents are so used to treat fabrics; their effectiveness is further developed by heating, which produces partial decomposition of the agent.

When two surfaces are to be bonded with an adhesive, both must be wet with the adhesive. Thus in applying stickers over varnished labels—tax stamps or price labels, for example —difficult wetting problems may be encountered which are similar to those occurring at the overlaps when varnished labels are applied to pasteboard boxes.

When the film of road dirt and oxidized lacquer is to be

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cleaned from the surface of an automobile by a cleanerpolish, the surface must first be wet, usually by a polyhydric alcohol but sometimes by a synthetic surface-active agent in solution. Similar but not identical problems with furniture polishes and glass cleaners are solved by the presence of alcohols and glycols, special soaps, sulfated alcohols, etc. Wetting of the skin by nonaqueous cosmetic creams is promoted by addi-

### INDUSTRIAL AND ENGINEERING CHEMISTRY



Courtesy, Doughnut Corporation of America

IN THE MANUFACTURE OF DOUGHNUTS, THE GREASE MUST HAVE THE PROPER SURFACE ACTIVITY; IF INSUFFICIENT THE DOUGHNUTS DO NOT PROPERLY BROWN; IF TOO GREAT THEY BROWN WITHOUT BEING DONE IN THE CENTER

tion of complex soaps or high-molecular-weight alcohols such as cetyl alcohol. Either promotes the removal of residues with soap and water.

An emulsion of saponifiable oil, which is barely stabilized with soap or sulfated oil, is used in the fat liquoring of leather. The stability is such that the emulsion breaks in the leather and deposits the oil inside the structure. This is the opposite of detergency, an application of the instability factor so dreaded in laundry practice and loosely termed "redeposition".

Surface-active agents have a function in aqueous solutions of insecticides, whether applied on plants or elsewhere. Soap is used in the majority of these products but cannot be applied with lime-sulfur or Bordeaux mixture, which require other surface-active agents. The functions of such agents in insecticides are (8):

To improve wetting, spreading, and penetrating properties.
 To increase initial retention, enhance tenacity, and ensure better coverage.

3. To reduce time and labor for application by combining treatments and permitting more rapid application.

In some cases weeds are killed but grass is not, due to incorporation of a surface-active agent which promotes wetting of the weed by a suitable solution.

In the treatment of oil wells with acid to increase their productivity, surface-active agents prove effective in promoting wetting and spreading. In lubricants they promote wetting of the metal surface, giving a film more difficult to dislodge. Incorporated in paper toweling, surface-active agents make the web more absorbent. Washing of papermakers' felts with calcium sequestration agents, such as the polyphosphates, is promoted by addition of surface-active agents to speed up penetration and wetting.

The applications of surface activity are not limited to aqueous solutions. In painting the figures on a clock or watch dial, the vehicle must just sufficiently wet the previously dried and usually molecularly oriented surface. It must not wet too readily or it will spread, it must wet sufficiently not to draw up into droplets, and it must adhere when dry. The same problem on a larger scale occurs in painting over a dried glossy surface; it is usually solved by removal of the superficial oriented surface by sandpapering. Physically this may give tooth, but physicochemically it provides a heterogeneous surface in place of an oriented one on which the new coat of paint is to be applied. An alternative is proper addition of wetting agents to the paint so that it will readily wet the oriented surface, penetrate it, and bond with it. Oxibeen expanded to the production of many other colors by displacement of water, the so-called flush colors or flush pigments. Castor oil was applied for grinding pigments for use in lacquer when the castor oil was intended to serve as plasticizer. This practice has been displaced; surface-active agents now serve to wet the pigment so that it can be readily incorporated.

Oil sorption by a paint pigment is an important property and is desirably as small as possible. Addition of a small amount of wetting agent reduces the amount of oil sorbed; the agent is sorbed by the pigment with its water-attracting groups outward, thereby repelling the oil. As an example, in the sorption of mineral oil by barytes, addition of less than 0.25 per cent of synthetic wetting agent reduced the oil sorption from about 16 to under 12 per cent (1). Another aspect of this problem occurs in paint grinding. It has long been known that addition of free fatty acid will assist in separation of the individual pigment particles, but because of their reactivity such acids cannot be used. Other surface-active agents have the same effect. Addition of 0.25 per cent of an alkyl pyridinium halide to raw linseed oil reduces the grinding time of red oxide of iron with an edge runner by one half. Subsequent dilution with oil reduces the surface-active agent to 0.05 per cent of the paint (1). In general, the wetting agents most effective in decreasing oil absorption are most effective in promoting dispersion.

At higher temperatures application of liquid metals to solid metals offers similar problems in galvanizing, soldering, or tinning. Wetting may be defeated by nonmetallic impurities on the surface or by molecular orientations which interfere. Agents as diverse as borax, zinc chloride, rosin, and crude palm oil which is high in palmitic acid, serve to wet the solid surface and promote wetting by the liquid metal.

At best these represent only isolated cases of surface activity as applied industrially. Whenever liquid-solid or liquid-liquid interfaces occur, surface activity is a factor. Even the reduction of corrosion in pipe lines by introduction of a sorbable material to prevent contact between the liquid and the pipe is an example.

#### Conclusion

By suitable combinations, with sufficient experimental work, a molecule can apparently be tailored to fit any surfaceactive requirement. Certainly great progress has been made in that direction. In 1941 a list of materials (16) by trade name, general type, and use numbered over 250; a current list more carefully edited (17) includes over 200. Such a

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dized oils are surface-active agents with respect to pigments and are often specific in their action. Too strong sorption of vehicle by pigment will cause gel formation in paints or inks, usually called "livering".

In the manufacture of white lead, preferential wetting by linseed oil has long been used to displace water and produce lead-in-oil without intermediate drying and grinding with oil. In recent years this has 35, Ka

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list inevitably contains many duplications, the same material appearing under different trade names. Also some borderline materials are more properly called "assistants" for surface-active agents, rather than surface-active agents except by the broadest definition.

To illustrate the multiplicity of these products, in a single patent of somewhat minor importance, nearly one hundred specific examples are discussed (6). Rarely is a patent issued in the field that does not permit of hundreds of variations. One of the longer patents (5) not only gives specific instructions for making forty-two different surface-active agents. but follows this with seven process claims and twenty-five broadly worded product claims. But however rapid the development of these products may be, it rests on the ancient foundation of soap manufacture and hardly justifies a statement recently made: "Surface-active compounds comprise a new group of organic chemicals just as do the vitamins, hormones, and dyes."

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PRESENTED before the Division of Colloid Chemistry at the 102nd Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

# **Pure Hydrocarbons** from Petroleum

### Vapor-Liquid Equilibrium of Methylcyclopentane-Benzene and Other Binary Aromatic Systems

### JOHN GRISWOLD AND E. E. LUDWIG<sup>1</sup>

The University of Texas, Austin, Texas

Atmospheric vapor-liquid equilibrium data for the system methylcyclopentane-benzene are presented. A minimum-boiling azeotrope exists at approximately 90 mole per cent methylcyclopentane.

Equilibria of binary systems containing aromatic hydrocarbons are discussed. It is evident that the presence of benzene prevents complete resolution of six-carbon petroleum fractions into their pure components by distillation, and that toluene greatly increases the difficulty of but does not prevent complete resolution of seven-carbon fractions.

IN AN ATTEMPT to separate the constituents of a sixcarbon fraction from natural gasoline by fractional distillation, two of the last components to distill were methylcyclopentane and benzene. It was found impossible to obtain pure methylcyclopentane by repeated fractionation in a Podbielniak Heli-Grid column (11), having an equivalent of more than sixty theoretical plates. These two hydrocarbons boil 9.3° C. apart, which is adequate for separation of normal mixtures by this column. An abnormality was apparent, and it was decided to investigate the vapor-liquid equilibrium of the binary system.

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### Vapor-Liquid Equilibrium of Methylcyclopentane-Benzene

MATERIALS. Phillips Petroleum Company and Shell Development Company furnished samples of methylcyclopentane. The physical constants indicated both samples to be of about the same purity. Since nitrating and sulfonating mixtures destroy the compound, it was purified by fractionation in the Podbielniak column, using total reflux and intermittent take-off. The charge volume was 390 cc. After the first 10 cc. were removed, boiling points and refractive indices of further samples were constant to within 0.1° C. and 0.0001 unit, respectively. Because of a very slow increase in refractive index in the fifth decimal place before that point, only the distillate from 170 to 320 cc. was used for the studies.

The benzene was The Barrett Company's 1° thiophenefree grade. It was fractionated through a laboratory column packed with 18 inches of glass helices, and a center cut of about 80 per cent of the original material was retained.

The physical constants of the purified materials are compared with some of the modern data from the literature in Table I. While the constants of highly purified methylcyclopentane have not been established with certainty, the values for the present material are congruent with the best data from the literature. For benzene, Wojciechowski's constants (21) are considered quite reliable. The present sample must

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MOL % METHYLCYCLOPENTANE IN LIQUID



MOL % METHYLCYCLOPENTANE

therefore contain an impurity not easily removable by distillation, such as cyclohexane. In this event the methylcyclopentane-benzene equilibrium will be slightly affected at high benzene concentrations. The influence of an equivolatile impurity must fade out as the benzene concentration is decreased, and the presence of a trace of cyclohexane will tend to reduce rather than to amplify the boiling point depression observed for the methylcyclopentane azeotrope.

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TABLE I. CON	ISTANTS OF M	ETH	YLCYCLOPENTANE	AND DENZENI
Literature Citation	B. P. at 760 Mm., ° C.		$n_{\mathrm{D}}^{20}$	d <sup>20</sup>
	Meth	ylcyc	opentane	
Original sample Purified sample (6) (22) (17) (14) (8) (19) (4) (18) (7)	71.8 71.9 71-72 71.9 71.9 72 71.8 71.9 71.8		1.40976 1.40972 1.4099 1.4100 1.40998 1.4100 1.4099 1.4099 1.4099 1.4098 1.4098	0.7477 0.7482 0.7496 0.7510 0.7496 0.7494 0.7494 0.7487 0.7453
		Benz	ene	
Purified sample (21)	80.1 80.094		1.50015 1.50122ª	0.8775 0.87896°
<sup>a</sup> Calculated fr	om values at 25	° C.	given in reference 2	1.

APPARATUS. Twenty-two equilibrium determinations were made in an Othmer apparatus (10), modified by the addition of a compensating wall heater, a glass check valve and drain in the liquid return line, and an ice water condenser on the vent. Boiling points were determined on twenty-five known mixtures in the apparatus of Willard and Crabtree (20), fitted with a four-junction iron-constantan thermocouple which was calibrated against the boiling points of pure compounds. Accuracy of the boiling point determinations was approximately 0.1° C. Analysis by refractive index was obtained with a Bausch & Lomb Precision oil refractometer having an accuracy of 0.00003 refractive index unit. Compositions of the equilibrium samples were determined from a plot of refractive indices at 20° C. of known mixtures. The data for the analytical plot are given in Table II.

**RESULTS.** The experimental data are summarized in Table II. The y-x plot (Figure 1) shows that the system deviates widely from ideality. The plot of relative volatility against composition (Figure 2) shows a definite dip below 1.0 at approximately 90 mole per cent methylcyclopentane, indicating an azeotrope. This plot is also a rather sensitive test for consistency of the data. The experimental boiling points (Figure 3) show a definite minimum at approximately 71.5° C. at the azeotropic composition. To prove the azeotrope, samples on both sides of its composition were boiled under total reflux in the Podbielniak column until equilibrium was attained. A small overhead sample was then withdrawn, and the still pot was cooled and sampled. The results are:

	Mole Fraction	Methylcyclopentane
Sample No.	Still pot	Overhead
$\frac{1}{2}$	0.0375 0.9500	0.8795 0.9038

### Behavior of Light Naphtha Hydrocarbons in Mixtures

The hydrocarbon classes present in light petroleum fractions are paraffins, naphthenes, and aromatics. In a strictly chemical sense, since these are all hydrocarbons they might be 100

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TABLE	II.	SUMMARY	OF	EXPERIMENTAL	DATA	ON	METHYLCYCLOPENTANE

Equilib	rium Dete	erminations	Boiling	Points	Known Mir	tures
Mole 1 methy per Liquid	leyclo- tane Vapor	Relative volatility, α	Mole fraction methylcyclo- pentane	° C. at 760 mm.	Mole fraction methylcyclo- pentane	n <sup>20</sup>
$\begin{array}{c} 0.0297\\ 0.1080\\ 0.1751\\ 0.3017\\ 0.8406\\ 0.4450\\ 0.5031\\ 0.5737\\ 0.6434\\ 0.7206\\ 0.7855\\ 0.8224\\ 0.8721\\ 0.9373\\ 0.9450\\ 0.9180\\$	$\begin{array}{c} 0.0526\\ 0.1668\\ 0.2533\\ 0.3870\\ 0.4598\\ 0.5179\\ 0.5673\\ 0.6255\\ 0.6795\\ 0.7442\\ 0.7986\\ 0.8299\\ 0.8499\\ 0.8499\\ 0.8754\\ 0.9034\\ 0.9034\\ 0.9034\\ 0.9034\\ 0.9174\\ 0.9287\\ 0.9360\\ 0.9442\\ 0.9503\\ 0.9505\\ 0.9602\\ \end{array}$	$\begin{array}{c} 1.814\\ 1.653\\ 1.598\\ 1.461\\ 1.385\\ 1.340\\ 1.295\\ 1.241\\ 1.175\\ 1.128\\ 1.083\\ 1.054\\ 1.046\\ 1.030\\ 1.005\\ 0.992\\ 0.988\\ 0.978\\ 0.988\\ 0.978\\ 0.988\\ 0.979\\ 0.971\\ \end{array}$	$\begin{array}{c} 0.0000\\ 0.0297\\ 0.1080\\ 0.1443\\ 0.1751\\ 0.3017\\ 0.3806\\ 0.4450\\ 0.5737\\ 0.6434\\ 0.7206\\ 0.8224\\ 0.8224\\ 0.8224\\ 0.9034\\ 0.9034\\ 0.9174\\ 0.9180\\ 0.9373\\ 0.9422\\ 0.9442\\ 0.9450\\ 0.9518\\ 0.9518\\ 0.9518\\ 0.9518\\ 1.0000\\ \end{array}$	$\begin{array}{c} 80.10\\ 79.64\\ 77.62\\ 77.15\\ 76.62\\ 74.85\\ 74.00\\ 73.43\\ 72.84\\ 72.06\\ 71.57\\ 71.53\\ 71.53\\ 71.47\\ 71.53\\ 71.47\\ 71.53\\ 71.66\\ 71.62\\ 71.62\\ 71.68\\ 71.80\\ 71.80\\ \end{array}$	0.0547 0.1343 0.1616 0.2095 0.3857 0.4851 0.6159 0.7486 0.7871 0.8336 0.8435 0.9366	$1.49333 \\ 1.48432 \\ 1.48120 \\ 1.47553 \\ 1.45794 \\ 1.44896 \\ 1.43820 \\ 1.42749 \\ 1.42749 \\ 1.42749 \\ 1.42175 \\ 1.42175 \\ 1.42138 \\ 1.41452 \\ 1.41$

expected to form ideal solutions. Fractions through the pentanes are separated in pure form by efficient fractional distillation. Hexane fractions have given considerable difficulty in the separation of their pure components (3), and in general the components in the pure state are not obtainable by fractionation alone. However, Bruun (5) was able to resolve almost completely a 55-65° C. cut into isomeric hexanes by distillation in 52-plate and 100-plate columns. Tongberg, Fenske, and Sweeney (15) reported in 1938 that no true constant-boiling mixture had been found in twenty virgin naphthas, although aromatic-nonaromatic mixtures behaved abnormally in distillation.

It is apparent that the presence of aromatics greatly interferes with separation by fractional distillation. The cut Bruun was able to resolve contained no aromatics. During the past few years, aromatics have been removed by nitration or azeotropic distillation before ultimate fractionation was attempted.

### **Binary Systems Containing Aromatics**

It has long been established that benzene-toluene form nearly ideal solutions. Toluene-xylene and the ternary mixtures with benzene do also (9). Beatty and Calingaert (1) reported that the toluene-ethylbenzene system is nearly ideal. On the other hand, all reported that aromatic-naphthene and aromatic-paraffin systems deviate widely from regularity of solution.

The existence of a benzene azeotrope with methylcyclopentane is established in this paper. Scatchard, Wood, and Mochel (13) took accurate isothermal data on the benzenecyclohexane system, which shows an azeotrope having a composition of approximately 50 mole per cent benzene at 70° C. Quiggle and Fenske reported data on the methylcyclohexane-toluene system (12). While it deviates greatly from ideality, it does not form an azeotrope. Tongberg and Johnston (16), studying the equilibrium of n-hexane-benzene, reported no separation obtainable at concentrations above 97 mole per cent hexane. Although a minimum-boiling mixture was not observed, the present authors are of the opinion that one exists having a boiling point within 0.1° C. of pure n-hexane, which thereby escaped detection. Otherwise this is the first pseudo-azeotrope to be established with modern fractionating equipment. Bromiley and Quiggle

(2) studied *n*-heptane and *n*-octane with toluene. No azeotropes formed, but the shape of both y-x curves was similar to that of methylcyclohexane-toluene, in that the relative volatility decreased abnormally as the composition approached the pure low-boiling component.

The existence of benzene azeotropes and the abnormally low relative volatility of toluene in certain concentrations with both lower and higher boiling compounds is considered an adequate explanation for the failure of good fractionation equipment to resolve six- and sevencarbon petroleum fractions into their pure components when aromatics are present.

### Acknowledgment

E. P. Schoch, of the Bureau of Industrial Chemistry, University

of Texas, generously loaned the distillation equipment and encouraged the work. Thanks are due George Scatchard for review and criticism of the manuscript.

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### Infrared Radiant Heating—Correction

It has been pointed out to the writers that a mistake in calculation arises in connection with Figure 8 on page 778 of the July, 1942, issue. The ordinate of performance should be multiplied by the factor 0.86. It should also have been specifically pointed out that the initial stock temperature was 80° F.

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# The Electron Microscope and Cellulose

### **R. BOWLING BARNES AND CHARLES J. BURTON**

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URING the past twenty or more years, numerous investigators have reported exhaustive studies relating to cellulose, its structure, and its physical properties. For example, Balls and Hancock (5) concluded that cotton fibrils were 0.4  $\mu$  in diameter. Herzog (11) reported a diameter of 0.3-0.5  $\mu$ , and Frey-Wyssling (10) found it to be 0.4  $\mu$ . Other workers, such as Freudenberg (9), Bailey and Kerr (4), Anderson and Moore (2), and Anderson and Kerr (1) expressed the opinion that fibrils have no consistent size and grade down to the limits of microscopic resolution. Seifriz and Hock (17) reported the existence of primary fibrils of  $1.4 \,\mu$  diameter and of secondary fibrils of  $0.1-0.3 \,\mu$  diameter. Farr and Eckerson (8) recognized the existence of ellipsoidal building units  $1.1 \times 1.5 \mu$  in dimensions. Recently Bailey and Brown (3) determined that the diameters of cellulose fibrils vary from 0.91 to 0.97  $\mu$ , depending upon the source of material. Many other scientists have made studies in this field, but the above citations serve to show the wide divergence of views which have been presented. Thus far, no common denominator has been found for these investigations, although heated controversies have frequently occurred in print.

It is not our intention to enter into these discussions. Our sole aim is to present a series of recently completed observations; the electron microscope has been used to photograph cellulose which has been mechanically disintegrated in water. At the same time a direct comparison is shown of photomicrographs and electron micrographs taken of exactly the same pieces of cellulose. It is believed that the pictures will be of considerable interest and help in connection with the proper interpretation of some of those published in the past by other authors.

The electron microscope has been described in detail in many papers, both scientific and popular; hence no such discussion need be given at this time. In a recent paper from this laboratory (6) a method was described whereby electronic magnifications as low as 160 diameters can readily be obtained without any appreciable loss of depth of focus or resolving power. These low magnifications make possible a direct comparison at the same magnification between optical and electron micrographs of the same specimen, and have proved of great value in a wide variety of electron microscopic studies.

The use of any optical instrument for the study of objects so small that they are comparable to or smaller than the limit of resolving power of the instrument is complicated by many factors. Among these is the fact that the depth of focus of the high-resolving-power objectives is of necessity so small (down to 0.06  $\mu$  for a theoretical resolving power of 0.15  $\mu$ ) that it is practically impossible to focus sharply at any one time more than a few scattered particles out of a given field. It can be understood that, while these few particles will be portrayed by the objective as accurately as possible, all others, whether larger or smaller will, if they do not have their largest cross sections accurately located in this shallow region

of sharp focus, give rise to images which are out of focus and greatly enlarged. Appreciable errors will also arise from the unavoidable presence in the image of diffraction effects. Inasmuch as cellulose fibrils and crystallites or particles have been reported to have diameters ranging from 0.1 to 1.4  $\mu$ . and since the limit of resolution of the best visible light microscopes is also of this same order of magnitude, we have believed that some of the chief characteristics of many published photomicrographs of cellulose have been determined by diffraction effects. The present study was therefore indicated. and the results show rather clearly that such has been the case.

### **Diffraction Effects and Optical Microscopes**

As a result of diffraction, each point in an object is portrayed by the objective lens as a disk surrounded by a set of faint rings, the diameter and appearance being a function of the wave length of light used and the geometry of the lens. The diameter of the central disk of the image is given by the expression:

 $d = \frac{2\lambda}{NA}$  (when object is illuminated by parallel light)

where  $\lambda$  = wave length of light used NA = numerical aperture of lens

Attention must be called to a fact important for the proper interpretation of the results shown; namely, the diameter of the small object does not enter at all into the expression giving the size of the diffraction image. It has been shown both theoretically and experimentally that these diffraction effects play a decisive role in limiting the resolving power of all optical instruments.

Rayleigh pointed out that two very small objects can just be revealed as a doublet when the centers of their images are far enough apart to cause the first diffraction minimum of one image to coincide with the center of the diffraction maximum of the other. Abbe showed that the practical limit of resolving power for a microscope can be expressed by the formula:

$$R = \frac{\lambda}{2n\sin\theta} = \frac{\lambda}{2NA}$$
 (oblique illumination)

- where  $\lambda$  = wave length of light, microns NA = numerical aperture of objective
  - = refractive index
  - R = distance between centers of two small particles which are just resolved

The maximum value of NA for any lens system used in air is slightly less than unity. If oil immersion objectives are used, NA can be made nearly equal to 1.5. Consequently, the best resolution which can be obtained is given by the expression:

$$R = \frac{\lambda}{2NA} = \frac{1}{3}\,\lambda$$

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FIGURE 1. COMPARISON OF PHOTOMICROGRAPHS (left) AND ELECTRON MICROGRAPHS (right) OF THREE OF THE SAME FIELDS OF CELLULOSE
Both micrographs were originally made at 1000 × but are enlarged here to 3000 ×. The photomicrograph was taken with green light, using a 4-mm. apochromatic objective, NA 0.95, depth of focus cs. 0.06 μ. In order to photograph the same field as that shown in the electron micrograph, the sample was allowed to remain on the nitrocellulose film suspended over a mesh opening in a metallic screen of 200 mesh per micrograph, the sample was allowed to remain on the nitrocellulose film suspended over a mesh opening in a metallic screen of 200 mesh per inch. These conditions used in electron micrography are not the optimum ones in photomicrography, and judgment of the photomicrograph should be made with consideration of the prevailing conditions. The intensities of the diffraction disks in the photomicrograph are proportional to the size of the diffracting point as shown in the electron micrograph.



FIGURE 2 (*Top*). Edge of Unfibrilated 15-Day Cotton FIBER ( $\times$  7500); Longitudinal Striation Is Apparent FIGURE 3 (*Center*). Material Leached Out or Washed FROM THE SURFACE OF 15-Day Cotton FIBERS IN WATER SUSPENSION ( $\times$  7500)

Figure 4 (Bottom). Portion of Cotton Fiber Which Has Swelled and Completely Lost Its Identity as a Result of Intense Electron Bombardment ( $\times$  7500)

For visible light of wave length 0.6  $\mu$ , the smallest resolvable distance will, therefore, be approximately 0.2  $\mu$ . By using ultraviolet light, this distance can be decreased by a factor of about 2.

In the case of single objects larger than this limit of resolution, the diffraction effects referred to above are superimposed upon the true refraction or absorption image. The resulting image, although conforming to the true shape of the object, will possess edges which are broadened by diffraction by an amount equal to R; this places a limit upon the accuracy with which the size of any given object may be determined.

The above discussion of diffraction disks can be shown (7, 12, 18) to hold, whether the small objects are themselves luminous, as in the case of stars, whether they are opaque particles, or whether they are transparent objects whose refractive index is different from that of the surrounding media. In fact, these objects need only be optical inhomogeneities in order to produce the diffraction phenomena referred to above. More complete treatments of this subject may be found in almost any standard textbook on optics. In these books, illustrations of the diffraction effects present in the images of stars, slits, needles, round opaque disks, etc., produced by both telescopes and microscopes, may be seen. Detailed discussions are given of the Fraunhofer and the Fresnel types of diffraction, as well as the reasoning and experiments which led to the above mentioned formula for resolving power.

For purposes of subsequent discussion, it need only be stated here that any minute object capable of absorbing, scattering, or diffracting light will be portrayed by a lens as an image in which diffraction will play an important role. As the size of the particular piece of matter which thus disturbs the light waves incident upon it decreases, the effects of diffraction become of greater importance in the production of the image, until finally the image is entirely produced by diffraction. While the size of such an image may be shown to bear no direct relation to the actual dimensions of the original particle, it is true that its relative intensity is a function of the particle size. From this point of view, accordingly, a field made up of a plurality of small pieces of matter whose centers are separated by a distance equal to or less than R will not be resolved by the particular objective used in calculating R. If, on the other hand, the field consists of objects separated by distances larger than R and varying in size about the value of R, the resulting field will be made up of a multiplicity of rounded-off images of varying intensities. While the larger, more intense images seem to have some definite shape, the others are almost round. The latter images vary downward in size until a certain minimum diameter is reached, and their intensities decrease until the images of the smallest particles fail to stand out against the general background.

Since the wave length associated with electrons, accelerated by a potential of 55,000 volts is, according to de Brogile, given by the expression

$$\lambda = \sqrt{\frac{150}{55,000}} \times 10^{-4} \,\mu,$$

and is equal to  $0.0000052 \mu$ , the electron microscope should be capable of resolving particles many times smaller than those which can be studied successfully in the optical microscope. It is well known that this is true. Objects have been clearly resolved by the electron microscope whose centers are separated by less than  $0.004 \mu$ . In these images the magnitude of the diffraction effects is extremely small. Therefore, if identical pieces of matter are photographed by both optical and electron microscopes, it should be possible to illustrate and determine the extent to which images produced by the light microscope are made up of diffraction effects. This has been done, and the photographs of cellulose shown in Figure 1 warrant particularly close and detailed examination.

### **Application to Cellulose Problems**

Since electrons are absorbed and scattered by air, the electron microscope must of necessity be operated at greatly January, 1943



FIGURE 5. FIFTEEN-DAY COTTON FIBER (× 6000) PARTIALLY (above) AND MORE COMPLETELY DISINTEGRATED (below) Two phases can be seen in each micrograph: a very dense material which is almost completely opaque to electrons, and an extremely fibrous material.

reduced pressures. For best results a vacuum corresponding to about 10<sup>-5</sup> mm. of mercury must be maintained. Thus, all specimens introduced into the microscope are strongly dehydrated. Furthermore, if the beam of fast-moving electrons incident upon the specimen is suddenly stopped by the object, an appreciable amount of heat is produced.

In view of these two effects, some doubt was entertained by the authors as to the applicability of the electron microscope to cellulose problems. A few preliminary attempts to examine whole cotton fibers confirmed our suspicions. Since cotton fibers are of the order of  $18 \mu$  in diameter, the heating effect was particularly bad. As soon as the mechanical stage was manipulated so as to bring a given fiber directly into the electron beam, the image on the fluorescent screen showed that the fiber underwent marked changes. Probably as a result of internal heating, the fiber would swell locally at several places. No satisfactory electron micrograph could be recorded since the swollen places were in a rapid state of motion. Sometimes they ran to and fro along the fiber, and at other times they swelled to many times the diameter of the original fiber and finally burst and collapsed. Once such a fiber had become thoroughly charred or burned, however, it would come to rest and further irradiation failed to produce additional changes.

Since experience has shown that thin sections must be of the order of  $0.1 \mu$  if satisfactory electron micrographs are to be obtained, little help could be expected from attempts at cross sectioning. One available technique, however, for minimizing the heating effects consisted of reducing drastically the intensity of the incident electron beam. Such a reduction obviously made proper focusing difficult but yielded encouraging results. Figure 2 shows an electron micrograph made in this way.

The most satisfactory results were finally obtained by subjecting the cotton fibers to mechanical disintegration prior to their introduction into the microscope. In this way the fiber fragments were reduced in diameter to a point where they were no longer opaque to the elec-By constantly observing the trons. large field visible in the intermediate image, it was easily possible to determine whether any changes in the appearance of the fragments took place as they were maneuvered into the electron beam. As a further check, optical photomicrographs were made of a given field both before and after the electron micrographs had been taken. In no case was any change in the appearance of such a finely comminuted specimen observed.

In making these studies, cotton fibers were taken directly from bolls, some 15 days old and others mature. These fibers were then suspended in water and subjected to the disintegrating action of a Waring Blendor for approximately 30 minutes. A drop of the supernatant liquid was then allowed to dry on a nitrocellulose or Formvar (polyvinyl

formal) membrane mount, following the usual technique of electron microscopy.

Figure 2 shows a portion of a whole fiber from a 15-day cotton boll. The sample was simply stirred in water, a suitable mount prepared, and the electron micrograph made at reduced electron beam current. Figure 3 was obtained from the same specimen mount as Figure 2. It shows material which has either been leached out of the fiber or washed from its surface. Figure 4 shows the effect of heat referred to above.

The electron micrographs in Figures 5 and 6 are typical of a great many fields which we have recorded. They show the appearance of both 15-day and mature cotton fibers which have been disintegrated in aqueous suspensions. The presence of two rather distinct phases, one fibrous and the other apparently amorphous and extremely opaque to electrons, is clearly seen.

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FIGURE 6. MATURE COTTON BOLL FIBERS MECHANICALLY DISINTEGRATED IN WATER ( $\times$  6000) Bundles of filaments are seen to be stripped from the large fiber at the lower left of the top micrograph.

### **Comparison with Photo**micrographs

Observations of these fields were made at 500 diameters with an optical microscope. In no cases did the optical images appear to be very similar to the electron images, which were usually observed on the fluorescent screen at about 6000 to 10,000 diameters. The reason for this apparent anomaly could not readily be ascertained, since it was never possible to know with certainty that exactly the same pieces of matter were being observed in the two microscopes. Accordingly (6) experiments were conducted as a result of which it became possible to obtain electron micrographs at low magnifications. By comparing directly photomicrographs and electron micrographs, as in Figure 1, the explanation for the lack of similarity is immediately apparent. From these comparisons it appears that the conclusions expressed in the introduction of this paper are correct. It can be shown that:

1. The chief characteristics of the optical image of these finely divided pieces of matter are a result of diffraction effects and the fact that many parts of the field are slightly out of focus. 2. Small pieces of either of the two

phases discussed above give rise to images very similar in appearance.

3. An apparent minimum "particle" size does exist in the cases of inhomogeneities smaller than the limit of optical resolving

4. In the case of the diffraction images, 4. In the case of the diffraction images, 4. In the case of the diffraction images, the intensities vary and decrease as the size of the objects decrease.
5. The smallest objects shown by the electron microscope fail to show up in the photomicroscope fail to show up in the shot opic shown in the sh

photomicrographs.

photomicrographs.
6. It is impossible to estimate accurately the size or the shape of such small objects from a study of their optical images.
7. Many types of inhomogeneities, such as the crossing or branching of filaments whose diameters are far below the limits of resolving power of the visual microscope, are blown up by different effects. are blown up by diffraction effects into rounded images which in some cases are many times too large. Similarly, minute objects or isolated bits of debris appear also as rounded and enlarged images.

In order to broaden the scope of this work, samples of cellulosic material from several other sources were prepared in a similar manner. Figures 7, 8, and 9 show typical fields of Whatman's grade 0 filter paper (mixture of cotton and wood cellulose), kraft pulp taken directly from a laboratory beater, and yellow pine sawdust. Apart from minor differences which can be explained by a consideration of the source of the material, all of our electron micrographs of cellulose show the same type of structure.

Attempts have also been made to disintegrate cotton fibers in other than water suspension. Almost no mechanical disintegration was found for cotton

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FIGURE 7. FILTER PAPER (WHATMAN'S GRADE 0) MECHANICALLY DISINTE-GRATED IN WATER ( $\times$  6000)

However, several of our electron micrographs are of special interest because they show direct comparisons with optical photomicrographs. The comparisons have been made primarily as part of a larger program of work undertaken to study the limitations of both optical and electron microscopy.

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FIGURE 8. KRAFT PULP AFTER HAVING PASSED THROUGH A LABORATORY BEATER ( $\times$  3250)



FIGURE 9. YELLOW PINE SAWDUST MECHANICALLY DISINTE-GRATED IN WATER ( $\times$  3250)

suspended in n-hexane, cyclohexane, benzene, and absolute alcohol, even when the disintegration was continued for long periods. Examination of the cotton after such treatments showed no signs of mechanical fibrilation.

### Conclusions

The work which we have briefly outlined has been done at various intervals during the past year. During that time, several papers, primarily of European origin, have been published on various phases of this same problem (13-16). Our results concur in general with those already published.

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# SURFACE-ACTIVE AGENTS'

## Manufactured in America and Commercially Available

NAME	TYPE	Uses	INDUSTRY	MANUFACTURER
Acidol	Fatty acid amine (tertiary)	Wetting	Textile, metal	Onyx Oil & Chemical Co., 15 Exchange Place, Jersey City.
Aciterge	Fatty acid salt of a substituted	Wetting, detergent	Metal, leather	N.J. Commercial Solvents Corp., Terre Haute, Ind.
Activol	oxazoline Alkyl aryl sulfonate	Wetting, detergent	Textile	Burkart-Schier Chemical Co., Chattanooga, Tenn,
Aerosol AS	Isopropyl naphthalene sodium sulfonate solution	Wetting in electro- lyte solns.	All	American Cyanamid & Chem- ical Corp., 30 Rockefeller Plaza, New York, N. Y.
Aerosol AY	Diamyl ester of sodium sulfosuc-	Same	Same	Same
Aerosol IB	Dibutyl ester of sodium sulfo-	Same	Same	Same
Aerosol MA	succinic acid Dihexyl ester of sodium sulfo-	Same	Same	Same
Aerosol OS	succinic acid Isopropyl naphthalene sodium sulfonate	Wetting, alkaline detergent assist-	Same	Same
Aerosol OT	Dioctyl ester of sodium sulfosuc-	Wetting	Same	Same
Ahco Penetrant L	Alkyl aryl sulfonate	Wetting, detergent	Textile	Arnold, Hoffman & Co., Inc., 55 Canal St., Providence, R. I.
Ahcowet SM Alframine DCA	Alkyl aryl sulfonate Sulfated glycerylamide	Wetting, detergent Detergent	Textile, leather Textile, laundry	Same Michel Export Co., Inc., 90 Broad St., New York, N. Y.
Aliphatic ester sulfate Alkamine SJ	Fatty acid ester sulfate Fatty amine	Wetting Detergent	Textile, pigment Textile	Onyx Oil & Chemical Co. Amalgamated Chemical Corp., Auburn & Trenton Aves., Bhiledelphia Panne
Alkanol B, SA, HG	Sodium alkyl naphthalene sul-	Wetting	Textile, paper, metal,	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
Alkanol S	Sodium tetrahydronaphthalene	Wetting, dispersing	All	Same
Alkanol WXN * Alox series	sulfonate Sodium hydrocarbon sulfonate Complex methyl esters of high- molweight alcohols, acids, & lactones	Wetting Wetting agents for metals & oils	Same Lubricating	Same Alox Corp., Buffalo & Iroquois Sts., Niagara Falls, N. Y.
Aminine S		Wetting, detergent	Textile, leather	Commercial Solvents Corp.
2-Amino-1-butanol 2-Amino-2-ethyl-1,3-				
propanediol 2-Amino-2-methyl-3-hexanol 2-Amino-2-methyl-1,3- propanediol	Fatty acid soaps of	Emulsifying	All	Same
2-Amino-2-methyl-1-propanol 2-Aminoethyl ethanolamine	Fatty acid soap of	Wetting, emulsify- ing	Same	Carbide & Carbon Chemicals Corp., 30 East 42nd St., New York, N. Y.
Ampo LA Aquatergent	Sulfated boro fatty acid amide	Wetting, detergent Detergent	Textile, leather Textile	Commercial Solvents Corp. Aqua-Sec Corp., 1450 Broad- way, New York, N. Y.
Arctic Syntex A	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH:CH(CH <sub>2</sub> ) <sub>7</sub> COOC <sub>2</sub> H <sub>4</sub> SO <sub>3</sub> Na	Detergent, wetting, emulsifying	Same	Colgate-Palmolive-Peet Co., 105 Hudson St., Jersey City. N. J.
Arctic Syntex M	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>10</sub> COOCH <sub>2</sub> CH(OH)- CH <sub>2</sub> OSO <sub>5</sub> Na	Detergent, wetting, emulsifying, dis- persing, lubricat- ing	Textile, laundry, paper, dyestuff	Same
Arctic Syntex M Liquid	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>10</sub> COOCH <sub>2</sub> CH(OH)- CH <sub>2</sub> OSO <sub>2</sub> NH <sub>4</sub>	Wetting	Cleaning	Same
Arctic Syntex T	$CH_3(CH_2)_7CH:CH(CH_2)_7$ $CON(CH_3)C_2H_2SO_3N_3$	Detergent, wetting, emulsifying	Textile	Same
Areskap	Monobutyl phenyl phenol so- dium monosulfate	Penetrant	Textile, embalming	Monsanto Chemical Co., St.
Aresket	Monobutyl diphenyl sodium	Wetting, spreading	Insecticides	Same
Aresklene	Dibutyl phenyl phenol sodium disulfonate	Emulsifying	Mold lubricant & pen-	Same
Arlacels A, B, C	Anhydrohexitol partial oleates	Same	Cosmetic, pharmaceu- tical	Atlas Powder Co., Wilmington, Del.

<sup>1</sup> Compiled by F. J. Van<sup>\*</sup>Antwerpen, Associate Editor, INDUSTRIAL AND ENGINEERING CHEMISTRY. Previous tables appeared in January, 1939, pages 66-69, and in January, 1941, pages 16-22.

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### SURFACE-ACTIVE AGENTS

NAME	Туре	Use	INDUSTRY	MANUFACTURER
Arylene	Alkylated aromatic sulfonate	Wetting	Textile	Hart Products Corp., 1440 Broadway New York N Y
Aurinol	Sulfated oleyl alcohol Sodium alkyl sulfates	Detergent, wetting Wetting	Textile, leather	Onyx Oil & Chemical Co. Du Pont Co.
Avitex AD Avitone A Besconol A	Sodium hydrocarbon sulfonate Monoethyl phenyl phenol so-	Emulsifying Detergent, wetting.	All Cosmetics	Same Beacon Co., 89 Bickford St.,
Beaconol M	dium monosulfonate Monoethyl phenyl phenol potas-	dispersing Same	Leather, paint, textile	Boston, Mass. Same
Beaconol S	sium monosulfonate Monoethyl phenyl phenol am-	Same	Leather, paper, paint,	Same
Beaconol T	inomonosulfonate Monoethyl phenyl phenol guan-	Same	textile Ink, paint, pigment	Same
Beta Sol	Quaternary ammonium salt	Wetting, dispersing	Textile	Onyx Oil & Chemical Co.
Betasol 01-A	acid Substituted amide of alkyl phos-	Wetting dispersing	Textile	ical Corp. Victor Chemical Works, 141
Cationic Agent C	phate (12-carbon)	weeting, dispersing	ACAthe	West Jackson Blvd., Chi- cago. Ill.
Cationic Agent D	Substituted amide of alkyl phos- phate (18-carbon)	Same	Same	Same
Cerfak	Alkylated aromatic hydrocarbon sulfonate (alkyl group is mixed dodaeyl radical)	Detergent	Same	E. F. Houghton & Co., 3rd, American, & Somerset Sts., Philadelphia, Penna.
Cominol	Salt of sulfonated higher fatty amide	Wetting, detergent	Same	Commonwealth Color & Chem- ical Co., Nevins, Butler, & Baltia Sta Brooklyn N Y
Darvan No. 1	Polymerized sodium salts of alkyl naphthalene sulfonic	Dispersing	Latex, paper, leather	R. T. Vanderbilt Co., Inc., 230 Park Ave., New York, N. Y.
Darvan No. 2	Polymerized sodium salts of sub- stituted benzoic alkyl sulfonic	Same	Same	Same
Daxad No. 11	Polymerized sodium salts of alkyl naphthalene sulfonic	Same	Synthetic rubber, pig- ment, textile	Dewey & Almy Chemical Co., Cambridge B, Mass.
Daxad No. 21	acids (alkyl short chain) Polymerized calcium salts of substituted benzoic alkyl sul-	Same	Gypsum, mining	Same
Daxad No. 23	fonic acids (alkyl long chain) Polymerized sodium salts of sub- stituted benzoic alkyl sulfonic	Dispersing, emulsi- fying	Paper, textile, flota- tion	Same
Daxad No. 27	acids (alkyl long chain) Compounded substituted ben- zoic alkyl sulfonic acids (alkyl	Dispersing	Sulfur, insecticides	Same
Deceresol OT	long chain) Dioctyl ester of sodium sulfosuc-	Wetting	Textile	American Cyanamid & Chem-
Detanol	Salt of sulfonated higher fatty amide	Wetting, detergent	Same	Commonwealth Color & Chem- ical Co.
Diethanolamine Diethylenetriamine	Fatty acid soaps of	Wetting, emulsify-	All	Carbide & Carbon Chemicals
Diethylethanolamine ) Dilex	Purified sulfolignin	ing Dispersing	Latex	Horn-Kem Corp., 43-42 Tenth St. Long Island City, N. V.
Dipex	Sodium salts of sulfonated petro-	Wetting, lubricat-	Textile, rubber mold lubricant	Stanco, Inc., 1 Park Ave., New York, N. Y.
Duponol C, D, ES, G, L-142, L-144, LS, ME, OS, WA,	Alkyl sulfates	Detergent, emulsi- fying, wetting	Paper, metal, pigment	Du Pont Co.
Dynesol K 50	Sodium salt of sulfated ester of	Penetrating	Textile	Amalgamated Chemical Corp.
Esterol	Sulfonated ester	Detergent	Textile	L. Sonneborn Sons, Inc., 88 Lexington Ave., New York. N. Y.
Gardinol LS	Sodium salt of technical oleyl sulfate	Detergent, wetting, emulsifying	Textile	Procter & Gamble Co., Ivory- dale, Ohio
Gardinol LS, WA, Special Gardinol WA, Special WA	Sodium alkyl sulfates Sodium salt of technical lauryl	Wetting, detergent Detergent, wetting, emulsifying	Same Same	Du Pont Co. Procter & Gamble Co.
Horn-Kem 1	Purified sulfolignin	Dispersing, flushing	Textile	Horn-Kem Corp.
Hytergen Igepal CA	Sulfated fatty acid amide Polyether alcohol condensate	Detergent Detergent, wetting,	Textile	Hart Products Corp. General Dyestuff Corp., 435 Hudson St. Norr Vork, N.Y.
Igepon AP Extra	Sodium sulfonate of oleic acid	Same	Same	Same
Igenon T	ester of aliphatic compound	Detergent	Same	Same
Integritol 65	Sulfonated alkylated benzene	Wetting, penetrat-	Paint, textile, leather	Hart & Harrington, Inc., 925 Weed St., Chicago, Ill.

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### SURFACE-ACTIVE AGENTS

	Trop	Use	INDUSTRY	MANUFACTURER
NAME	1 TPE		Tratile mubber nig-	Synthetic Chemicals, Inc., 57
Intracol .	Long-chain fatty acid basic amide	Dispersing, wetting	ment	Wilkinson Ave., Jersey City, N. J.
Intrals 222, 231, 233	Polyethers	Wetting, dispersing, emulsifying	Same	Same
Intramine	Sodium salt of sulfonated lauryl & myristyl collamide	Detergent, wetting	Textile, metal, rubber	Same
Invadine B, C, N	Alkyl phenylene sodium sulfon- ate	Wetting	Bleaching, carboniz- ing	Station C, New York, N. Y. Swithetic Chemicals, Inc.
Janusol	Cation- & anion-active com- pound	Dispersing, emulsi- fying, wetting	ber Tertile	Arkansas Co., Inc., Newark,
Lanitol P, S	Sodium alkyl aryl sulfonate	Detergent	Textile	N. J.
Leonil SA	Alkyl naphthalene sodium sul- fonate (alkyl group lower than heyyl)	Wetting, dye	Same	General Dyestun Corp.
Lightning Penetrator X	Salt of sulfated higher alcohol	Wetting, penetrant	Same	ical Co.
Lupomin	Fatty acid amide salt	Emulsifying		N. J.
Mapro Degum	Sulfated cetyl alcohol and auxili- aries	Detergent	Textile	Some
Maprofix	Sulfated cetyl alcohol	Same Wetting	Same	Same
Mapromin Mapromol	Sulfated oleyl alcohol	Same	Textile, leather	Same
Mercerol		Same	Textile	61 Van Dam St., New York, N. Y.
Merpentine	Sodium alkyl naphthalene sul- fonate	Wetting	Textile, leather	Du Pont Co.
Merpol B, C	Sodium alkyl sulfate	Wetting, detergent	Textile, leather, paper	Same Same
Modinal D, ES Modinal D, ES	Sodium alkyl sulfates Sodium salt of technical lauryl	Detergent, wetting, emulsifying	Same	Procter & Gamble Co.
Monoethanolamine	Fatty acid soap of	Wetting, emulsify-	All	Carbide & Carbon Chemicals
Morpholine J Mulsor		Emulsifying, lubri-	Insecticide, textile,	Synthetic Chemicals, Inc.
MP-189, Flakes, -S	Sodium hydrocarbon sulfonate	Wetting, dispersing, detergent	All	Du Pont Co.
N-25	Alkylol amine	Detergent	Developmine	E. F. Houghton & Co.
Naccolene F	Modified alkyl aryl sulfonate	Same	Dry cleaning	Co., Inc., 40 Rector St., New York, N. Y.
Nacconol E	Sodium alkyl aryl sulfonate	Same	Fruit washing	Same
Nacconol EP Nacconol NR	Same	Detergent, dyeing,	Cleaning	Same
142000001 1124		wetting		0
Nacconol NRNO	Same	Detergent Same	Laundry	Same
Naccosol A	Sodium alkyl naphthalene sul-	Wetting	Textile	Same
Negamine	Cation-active amino esters of	Dispersing, wetting	Textile, pigment, rub-	Synthetic Chemicals, Inc.
Nekal A	Sodium alkyl naphthalene sul-	Wetting, emulsify-	Textile, pigment,	General Dyestuff Corp.
	fonate (alkyl group lower than hexyl)	ing	paint	
Nekal BX	Isobutyl naphthalene sodium sulfonate	Wetting, dye leveler	Textile	Same
Neomerpin N	Alkyl naphthalene sulfonic acid	Carbonizing, wet- ting	Textile	Du Pont Co.
Neutronyx	Nonionic fatty acid condensate	Dispersing, emulsi- fying	All	Onyx Oil & Chemical Co.
Ninol 737	Mixed fatty acid (C <sub>10</sub> -C <sub>16</sub> ) alkyl- olamine condensate	Wetting, detergent	Textile, fur, laundry	Ninol Laboratories, 638 South Federal St., Chicago, Ill.
Ninol 400	Same Hevitan partial fatty acid ester	Detergent	Textile, metal	Same
Nopco 1067	Long-chain alkyl aromatic sul- fonate	Detergent	Textile	Atlas Powder Co. National Oil Products Co., Inc., Harrison N J
Nopco 1073-B	Oleic amine ester Short-chain aliphatic ester sul	Emulsifying		Same
Nopco 1080-D	fonate	weiting		Same
Nopco 1807-C	Short-chain alkyl aromatic sul- fonate	Wetting	Textile	Same
Nopco CVT	Oleic amine Sulfonated oleic amino	Same	Ceramics	Same
Novonacco	Modified sodium alkyl naphtha-	Wetting	Textile	Same National Anilina & Chamical
	lene sulfonate			Co., Inc.

January, 1943

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### SURFACE-ACTIVE AGENTS

NAME	Type	Use	INDUSTRY	MANUFACTURER
Novonacco NN	Modified alkyl naphthalene sul-	Wetting, carboniz-	Same	Same
NSA.E.	fonic acid Isopropyl naphthalene sulfonate	Wetting	Textile, agriculture	Onyx Oil & Chemical Co.
Oleo Glycerol Sulfate	Fatty ester sulfate	Wetting, dispersing	Textile	Same
Onvrsan C. O. S	Alkyl amidoalkyl imidazoline	Same	Textile, leather	Same
Oranap	Alkyl naphthalene sodium sul- fonate	Wetting, detergent	Textile	Jacques Wolf & Co.
Oratal	Sulfonated amide	Same	Same	Same
Orthocen K	Sulfonated higher phenol	Penetrating, wet- ting	Same	American Aniline & Extract Co., F & Venango Sts., Philadelphia, Penna.
Orvus WA	Sodium salt of technical lauryl	Detergent, emulsi-	Laundry, rubber, metal insecticide	Procter & Gamble Co.
Penequik	Sulfonated ester	Wetting, penetrat-	Textile	L. Sonneborn Sons, Inc.
Penetrol 60	Sodium and potassium salts of sulfonated esters of dicar-	Wetting, penetrat- ing	Paper, textile, leather	Beacon Co.
Penetrol 65	Sodium and potassium salts of	Same	Same	Same
Penetrolin AC	sulforicinoleic acids Sodium salt of alkylated naph-	Wetting	Textile, leather	Arkansas Co., Inc.
Pentamul 6	thalene sulfonic acid Pentaerythritol monostearate	Emulsifying	All	Heyden Chemical Corp., Gar-
		0	Zamo	neid, N.J.
Pentamul 9 Pentamul 87	Pentek monocaprate Pentaerythritol soybean fatty	Same	Same	Same
	acid monoester	Q	Sama	Same
Pentamul 88	Pentek monolaurate	Same	Same	Same
Pentamul 126	Pentaerythritol monooleate	Same	Same	Same
Pentamul 145	Pentek monostearate	Same	Same	Same
Pentamul 147	Pentaerythritol monolaurate	Same	Same	Same
Pentamul 149	Pentaerythritol monocaprate	Watting	Textile leather	Onyx Oil & Chemical Co.
Phi-¢-Sol W. A. Quaker Dianol D	Sulfonated higher alcohol &	Wetting, detergent	Textile	Quaker Chemical Products Corp., Conshohocken, Penna.
Quaker Pro-So-Tex 55	Aromatic sodium sulfonate	Wetting	Textile, oil compound-	Same
0 1 D . C. Ter 59	Sulfonated natroleum derivative	Same	Textile	Same
Quaker Pro-So-Tex 58	Alleylated arvl sulfonate	Detergent, wetting	Same	Same
Quaker Fro-So-Tex 75	Sulfonated fatty acid	Wetting	Textile, paper, leather	Naphthole, Inc., Boonton, N.J.
Quixite	Same	Detergent	Textile, leather	Same
Ramol P. W.	Condensation product of sul-	Dispersing	Pigment	Jacques Wolf & Co.
Populin B	Substituted hydrocarbon	Wetting	Textile	Sandoz Chemical Works, Inc.
Resolin N F	Same	Same	Leather	Same
Rinfors L.		Detergent	Textile	Same
Sandonan A		Detergent	Same	Same
Sandozol N		Wetting	Same	Same
Santol S	Aryl sodium sulfonate	Same	Same	Charlotte Chemical Labs., Inc., Charlotte, N. C.
Santomerse	Alkylated aryl sulfonate	Wetting, detergent,	All	Monsanto Chemical Co.
0	Alley and amine sulfanate	Wetting, dispersion	All	Same
Santomerse 43 Sapamine A	Diethyl aminoethyl oleyl amide		Textile	Ciba Co., Inc.
Soapotol	Salt of sulfonated higher fatty	Wetting, detergent	Same	Commonwealth Color & Chem- ical Co.
	Alleriated and sulfariate	Wetting	Same	Ciba Co., Inc.
Solvadine NC Conc.	Alkylated aryl sulfonate	Emulsifying	Soluble oil	Stanco, Inc.
SP-315 SP-717	Same	Dispersing, emulsi-	Paint, pigment	Same
Span 20	Sorbitan monolaurate	Emulsifying, wet-	Food, textile, leather	Atlas Powder Co.
Span 40	Sorbitan monopalmitate	Emulsifying	Paper, laundry	Same
Span 60	Sorbitan monostearate	Same	Cosmetic, food	Same
Span 80	Sorbitan monooleate	Same	All	Same
Span 85	Sorbitan trioleate	Same	1 extile	Havester Com Malross
Stablex A	Naphthalene sulfonate	Wetting	Latex	Mass.
Stabler C		Same	Same	Same
Stablex G	Petroleum sulfonate	Same	Same	Same
Stearony	Quaternary ammonium halide	Same	Textile, agriculture	Unyx Ull & Chemical Co.
Sulfamine	Sulfated amine	Detergent		L. Sonneborn Sons, Inc.
Sulfanole	Sulfated fatty acid amide	Same	Textile	Warwick, R. I.
Sulfatate	Sodium salt of sulfonated hydro- carbons	- Wetting	Textile, paper, cos metic, leather	<ul> <li>Glyco Products Co., Inc., 14 Lafayette St., New York N. Y.</li> </ul>

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### SURFACE-ACTIVE AGENTS

NAME	TYPE	Use	INDUSTRY	MANUFACTURER
Supersulfate F. S. Powder	Sulfated aryl alcohol	Wetting, detergent	Textile	Laurel Soap Mfg. Co., Inc., Tioga, Thompson, & Almond Sts., Philadelphia, Penna.
Surfax W. O. Tensol	Highly sulfated fatty ester Sulfonated naphthalene alkyl	Wetting Wetting, dispersing	Same Textile, pigment, rub- ber flotation	E. F. Houghton & Co. Synthetic Chemicals, Inc.
Tergitol Penetrant 08 Tergitol Penetrant 4 C.H.	ether $C_4H_9CH(C_2H_6)CH_2SO_4Na$ $_9CH(C_2H_6)C_2H_4CHCH_2CH(CH_2)_2$	Same Same	Same Same	Carbide & Carbon Chemicals Corp. Same
Territol Penetrant 4T	 SO4Na Triethanolamine derivative of	Same	Same	Same
Tergitol Penetrant 7 C.H.	7-ethyl-2-methyl-4-undecanol CH $(C_2H_6)C_2H_4CHC_2H_4CH(C_2H_6)_2$	Same	All	Same
	SO4Na			
Tetraethylene pentamine	Fatty acid soap of	Wetting, emulsify- ing	Same	Same
Tetranol 1638 Texol Titadine T. A.	Sulfonated fatty ester Fatty acid condensate Mixture of alkyl naphthalene sulfonic acid ester & sulfated	Wetting Wetting, detergent Wetting	Textile, leather Textile Same	Burkart-Schier Chemical Co. Titan Chemical Products, Inc., Mill Road & Wayne St., Jersey City, N. J.
Titamine T. C. P.	Derivative of sulfonated alcohol	Wetting, emulsify-	Same	Same
Titan Decitrene	Alkylated aromatic sulfonate	Wetting	Same	Same
Titanole R. M. A.	Alkylated aryl sodium sulfonate	Same	Same	Same
Titascour	Sodium salt of sulfonic acid	Wetting, detergent	Same	Same
Titazole S. A.	Sodium alkyl naphthalene sul-	Wetting	Same	Same
Triethanolamine	fonate Fatty acid soap of	Wetting, emulsify-	All	Carbide & Carbon Chemicals Corp.
Tris(hydroxymethyl) amino-	Same	Same	Same	Commercial Solvents Corp
Triton 720	Sodium salt of aryl alkyl poly- ether sulfonate	Detergent, wetting	All	Röhm & Haas Co., Inc., 222 West Washington Sq., Phila- delphia, Penna.
Triton 770	Sodium salt of aryl alkyl poly- ether sulfate	Wetting, emulsify- ing, dispersing, detergent	Cleaning	Same
Triton E-79	Amine salt of alkyl phenolic other sulfate	Wetting, emulsify-	Textile, paper	Same
Triton K-60	Cetyl dimethyl benzyl ammo- nium chloride	Wetting, dispersing	Textile	Same
Triton NE	Aryl alkyl polyether alcohol	Detergent, wetting	Textile, ceramic, elec- troplating	Same
Triton W-30	Sodium salt of aryl alkyl ether	Wetting, dispersing, penetrating	Textile, paper, leather, laundry	Same
Turco Acidose	Alkyl aryl sulfonate	Wetting	Steel, petroleum	Turco Products, Inc., 6135 South Central Ave., Los An- geles, Calif.
Tween 20	Polyoxyalkylene ether of partial lauric acid ester	Emulsifying, wet- ting, dispersing, detergent	All	Atlas Powder Co.
Tween 40	Polyoxyalkylene ether of partial palmitic acid ester	Same	Same	Same
Tween 60, 61	Polyoxyalkylene ether of partial stearic acid ester	Same	Same	Same
Tween 80, 81, 85	Polyoxyalkylene ether of partial oleic acid ester	Same	Same	Same
Ultravon K, W	Sulfonated complex stearyl alkyl compound	Detergent	Textile	Ciba Co., Inc.
Ultrawet, 40	Alkylated monosodium benzene sulfonate (several alkyl groups total 10 carbon)	Wetting, detergent	Textile, laundry, agri- culture, paint	Atlantic Refining Co., 3144 Passyunk Ave., Philadel- phia. Penna.
Unitex	Sodium salt of alkylated aro- matic sulfonate	Wetting, detergent	Textile	Commonwealth Color & Chem-
<b>W. A. 35A, B,</b> C	Phosphorated higher alcohol (octyl),Na <sub>5</sub> P <sub>5</sub> O <sub>20</sub>	Wetting, penetrat-	Textile	Victor Chemical Works
W. A. 58	Phosphorated higher alcohol (capryl) NapPeO20	Same	Same	Same
Warcosol	Isopropyl naphthalene sodium sulfonate	Wetting	Same	Warwick Chemical Co.
Warcosol 897	Long-chain alkyl sodium sul- fonate	Same	Same	Same
Wetanol	Modified sodium salts of sul- fated fatty alcohols	Same	Textile, paper, leather	Glyco Products Co., Inc.
Wetsit Wetting Agent 5-21	Alkylated aromatic sulfonate Mixt. of hydrocarbon sulfonate & a substituted aminodioxane	Same Wetting, detergent	Textile, paper Textile, leather	Jacques Wolf & Co. Commercial Solvents Corp.
Xynocol Xynomine	Sulfated fatty acid amide	Wetting, detergent	Textile	Onyx Oil & Chemical Co.

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### Three sure things

In 1943 Uncle Sam will need huge quantities of 100-octane gasoline for our fighting flyers, toluene for explosives and synthetic rubber to keep military and essential civilian wheels rolling

We don't know just how much will be needed but these three things we do know

- 1. There is enough petroleum to supply the components of these vital products in enormous volume
- 2. U.O.P. processes are ready to produce them from that petroleum efficiently and speedily, and those processes are at the service of all refiners under license from Universal
- 3. U.O.P. know how, built up in a quarter century of experience, is exclusively devoted to helping the refining industry achieve the greatest possible war production—till victory is won

## Happy New Year

OIL IS AMMUNITION - USE IT WISELY

Universal Oil Products Co Chicago, Illinois



Dubbs Cracking Process Owner and Licensor

THE REFINERS INSTITUTE OF PETROLEUM TECHNOLOGY

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## Condenser tubes and plates for war processes

Fortunately, we have a Navy that wants, and gets, the best. For its warships, the Navy favors cupro-nickel condenser tubes made by the extrusion process. For prior to any finishing operation, an extruded tube is a sound, clean, dense piece of metal with an excellent surface . . . the kind of condenser or heat exchanger tube that can help to keep your own processes free from operating tie-ups and delays.

Years before the extrusion process for making condenser tubes became general practice, Revere began using this method. And the secondary processing of Revere tubes imparts further desirable characteristics for dependable service. Revere tubes have behind them an unusually long and valuable experience in these modern manufacturing methods.

Revere tubes and sheets are produced in a range of alloys meeting every requirement of industry at war. The Revere Technical Advisory staff is always ready to help with difficult problems.



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The remaining short Butt end of the Billet is sheared off from the extruded tube.







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For most jobs in the process industry, AO Duralite Chemical Goggles are especially recommended. Super Armorplate Lenses provide resistance to flying chips. Solid baffle-plates in back of the side shields protect the eyes against splashing chemicals. Slots in the lens rings and radial slots in the eye cups and side shields insure ample ventilation to keep eyes cool and prevent the inside of the lens from lens fogging. Above all, these goggles are light in weight, snug-fitting, and unusually comfortable to wear.

Ask your AO Safety Representative to demonstrate the remarkable features of the AO Duralite Chemical Goggle.



SOUTHBRIDGE, MASSACHUSETTS

# Laboratory work on synthetic rubber is done ON Alberene Stone surfaces

Alberene Stone has been standard equipment for working surfaces in good laboratories for fifty years. Popularity and leadership have been maintained by durability, performance and economy. Despite unusual demands for table-tops, fume hoods, sinks, tanks, drainboards, etc., due to the War, unlimited supplies of non-critical soapstone and ample fabricating facilities enable us to make prompt shipments.

Typical of the manufacturers of synthetic rubber to whom we have furnished Alberene Stone laboratory equipment are Goodyear Tire & Rubber Co., E. I. du Pont de Nemours Co., Standard Oil Development Co., etc.

Recent installations have been made in vitally important laboratories in the metal, chemical and oil industries, and for every branch of the Government, also.

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# WELDING AND BRAZING ALCOA ALUMINUM

Here's a book of data designed to meet the needs of the practical man—the welder—who is working with Aluminum Alloys. It describes in detail the practices now widely employed for joining Aluminum parts by gas welding, arc and resistance welding, and by brazing.

This book is planned to assist the war effort by making every welder more proficient at his job. Typical subjects covered are: Welded joint design—preparation of parts—types of welding equipment—electrodes and fluxes—tip selection and flame adjustment—inspection and finishing—strengths of welds.

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### "dag" COLLOIDAL GRAPHITE AS A HIGH TEMPERATURE LUBRICANT

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"dag" colloidal graphite is not only an excellent lubricant at normal temperatures but it is unique in retaining its lubricating properties at elevated temperatures. It remains unaffected after its liquid lubricant carrier has been completely burned away. Remaining on the heated surfaces. it protects them from abrasive wear.

"dag" colloidal graphite particles are so small they readily pass through the microscopic pores of filter paper. When dispersed in a liquid, oil, for instance, these particles of colloidal graphite be-come practically an integral part of the oil and are carried wherever it spreads or penetrates. Consequently, all elements of a mechanism lubricated by "dag" colloidal graphite in oil are uniformly covered with a graphite film. This is not true of powdered graphite because of its very much larger particle size and its in-ability to remain in suspension.

Also, because of the extreme smallness of colloidal particles, "dag" dispersions,

ACHESON

properly diluted, will not clog lubricators, oil lines, or oil grooves. "dag" colloi-

dal graphite in oil may be used in any type of lubricating system without interfering with its proper functioning. "dag" colloidal graphite is being used with complete success to lubricate the bearings and rubbing surfaces of oven and furnace conveyors, kiln cars, forging dies, hot piercing tools, electric toasters, high intensity searchlights, Cottrell precipitators, lehrs, movie projectors, and the moving parts of die casting machines -also in the lubrication of glass and rubber molds.



### **Difference Between Colloidal** and Powdered Graphite

Corp. (7) The verdict of the judges will

be final.

"dag" colloidal graphite dispersions should never be confused with dispersions of powdered graphite which have not the same properties. "dag" colloidal graphite particles are many times smaller than the particles of powdered graphite —so small they readily pass through the smallest pores of filter paper. In fact, they go wherever their liquid carrier penetrates. The carefully controlled Acheson process of colloidalization imparts to these particles a property powdered graphite does not have. This is "Brownian Movement" which enables colloidal graphite to remain in suspension indefinitely.

"dag" is a registered trade-mark of the Acheson Colloids Corporation.

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# "ONE TINY PART of the SYNTHETIC RUBBER INDUSTRY"



Charged with Activated Alumina for efficient, dependable drying, these Lectrodryers are on their way to a synthetic rubber plant.

This comment about these huge Lectrodryers— "one tiny part..."—compares them to the gigantic new synthetic rubber plants. Actually, these machines loom big in importance because drying is a vital step to our new source of rubber.

Vitally important, too, is the dependability and high efficiency of the drying agent with which these machines are charged. Alorco Activated\* Alumina does its drying job well, no matter what the assignment; drying liquids, air, or gases to dew points below -110° F. And Activated \*Registered trade mark Alumina removes acids from oils and other liquids.

When Activated Alumina becomes laden with moisture, it is reactivated by heating and restored to its original high efficiency.

Alorco Activated Alumina is providing dependable drying service on all kinds of war work; increasing yields and recoveries; maintaining constant quality; eliminating corrosion and assuring continuous performance of equipment.

ALUMINUM COMPANY OF AMERICA (Sales Agent for Aluminum Ore Company) 1911 Gulf Building, Pittsburgh, Pennsylvania.

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### INSTALLED WITH STANDARD EQUIPMENT

Some pipe can be threaded with standard pipe threading tools. Welding operations are simple and rapid, requiring hardly more than 45 seconds for the entire process. Welded joints possess strength equal to that of the pipe itself. Saran pipe fittings are rapidly becoming available. Complete technical information is contained in free booklet "Saran Pipe."

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### SARAN PLASTIC PIPE Replaces Strategic Materials Adds New Advantages

With American war production at an all time high, saran pipe is proving invaluable as a replacement for urgently needed metal and rubber. It is ready to go to work in widely diversified capacities—for chemical processing plants, rayon, paper, oil, gas and other industries.

But this Dow plastic development is far more than a "war replacement." It is new and revolutionary—the first thoroughly practical thermoplastic pipe.

Saran pipe is tough and durable. Exceptional chemical resistance gives it special value wherever corrosion and exposure conditions are severe. Moreover, saran pipe is only <sup>1</sup>/<sub>4</sub> the weight of comparable sizes of iron pipe, a factor of definite importance in shipping, general handling and suspension.

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CHEMICALS INDISPENSABLE TO INDUSTRY AND VICTORY

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ELLIOTT Steam Jet EJECTORS

# Steam with the speed of bullets - and aimed at the axis, too

Steam jets travelling at 3600 feet per second, and more, are pulling vacuum for the manufacture of explosives. These jets are the moving element (and the only moving element) in Elliott steam jet ejectors.

Hundreds of Elliott single-stage and multi-stage ejectors are putting their fast-moving steam jets behind Uncle Sam's drive for victory, not only in making explosives, but also in manufacturing magnesium, and synthetic rubber, producing high octane gasoline, drying blood plasma. Some processes require handling large volumes, some small. Some use extremely high vacuum, others relatively low. All of these conditions are easily met by various sizes and arrangements of ejector stages, with or without intercondensers. Elliott ejectors are not only the simplest type of vacuum pump, but also the most versatile.

Have you a vacuum problem? Consult with us.



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Steam Jet Ejector Dept. JEANNETTE, PA. DISTRICT OFFICES IN PRINCIPAL CITIES January, 1943

The Chemist is Today's Crusader Against Short Rations 53

New processes of dehydration provide just one illustration of the vital importance of the chemical laboratory in the world-wide problem of food supply.

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25	1/10	2	1.75
50	1/10	2	1.75
100	1/5	2	2.53
	Capacity ml. 10 25 50 100	Capacity         Subdivision           ml.         ml.           10         1/20           25         1/10           50         1/10           100         1/5	Subdivision         Stapcock           ml.         ml.         Size           10         1/20         2           25         1/10         2           50         1/10         2           100         1/5         2

For quantity prices, and for details about Kimble hurettes of all types and for all purposes, consult your dealer.

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Steam

# with the speed of bullets. - and aimed at the axis too

Steam jets travelling at 3600 feet per second, and more, are pulling vacuum for the manufacture of explosives. These jets are the moving element (and the only moving element) in Elliott steam jet ejectors.

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January, 1943

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### CONTROLS FOR

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For the past few years, Bristol engineers have worked closely with the designers of synthetic rubber processes. Today, the automatic control instruments developed during that period of collaboration are ready to insure the day-by-day precision of a vast, new war-essential industry.

Bristol instruments, engineered under pilot plant conditions, are now in full-scale operation, controlling temperatures and pressures, flow and flow ratios, pH values, and the *time cycles* that guide and guard the process at every step.

Complete descriptions of Bristol installations, now at work to meet the rubber crisis, are available on request from qualified executives. Automatic Control of Catalytic Dehydrogenation Process "The Catalytic Dehydrogenation Process" — by Grosse & Ipatieff.

### IN OTHER INDUSTRIES, TOO - UNVARYING REPETITION OF DESIRED CONTROL SCHEDULES

Many firms have found that individual instruments, however perfect, are not sufficient in themselves, but need a complete control system engineered for the particular process. Bristol's Coordinated Process Control, insuring the unfailing, mechanical repetition of proven best procedures, often increases the value of an entire instrument investment, sometimes paying for itself within a few months. Write The Bristol Co., 109 Bristol Road, Waterbury, Connecticut.

### THE BRISTOL COMPANY WATERBURY, CONNECTICUT

The Bristol Co. of Canada Ltd.
## Automatic Controls for Synthetic Rubber Processes



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Write for Bulletin 103 on Bristol Controls for Synthetic rubber production.

### BRISTOL'S POLYMERIZER CONTROL SYSTEM SIMPLIFIES PRODUCTION OF SYNTHETIC RUBBER

Simplicity of automatic temperature control, with all possible elimination of hand adjustment, was found essential for polymerization of butadiene and copolymers such as styrene or acrylonitrile.

A single instrument of simple construc-

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Pressed elbows, tapering from 30 inches to 25 inches diameter, made from 4 inch plate, connected to header. Design pressure, 1475 lb. per sq. in.



Vessel shown is built of Croloy 2 plate, with streamlined openings — for service at 100 lb. per sq. in. and 1050 F.





# **B&W** process equipment solves problems of temperature and pressure

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More than two million pounds of B&W Alloy Tube Support Castings have been supplied for service temperatures as high as 2000 F., where high creep strength is required. Not a service failure has been reported.



**B&W STREAMLINED OPENINGS** All reinforcing is forged and drawn from parent metal. Concentration of stresses is avoided.

## Do You Know These Facts About HASTELLOY ALLOYS... For Resistance To Severely Corrosive Media?

For resistance to severely corrosive media, use one of the four Hastelloy nickel-base alloys – A, B, C, or D. Many types of chemical equipment—such as valves, pumps, pipe and fittings, autoclave liners, heating or cooling coils, agitators, and acid concentrator tubes — are being fabricated from these high-strength alloys. Outlined here are some of their properties.





For Complete Information on penetration tests, available forms, and methods of fabrication of Hastelloy alloys, send for the booklet, "Hastelloy High-Strength Alloys." Test samples of these nickelbase alloys are also available.

HAYNES STELLITE COMPANY Unit of Union Carbide and Carbon Corporation New York, N. Y. Kokomo, Indiana Chicago, Cleveland, Detroit, Houston, Los Angeles, San Francisco, Tulsa

HIGH-STRENGTH NICKEL-BASE ALLOYS FOR CORROSION RESISTANCE

January, 1943

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COMPLETE VALVE CROSS SECTION SHOWN BELOW

GET IN THE CRAP

STAINLESS STEEL LINERS SAVE METAL

Voqt GATE VALVE AND SLIDE VALVE TYPES AVAILABLE

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The War Program demands conservation of all strategic metals that are vital to victory. Therefore, by specifying stainless steel lined valves in flow \* control services involving severely corrosive-erosive or high temperature liquids and gases, as much as 75% of the vital metal can be saved . . . a definite contribution to the war effort!

Vogt stainless steel linea drop forged steel gate and slide valves are serving today in many applications throughout industry. Liners of the stainless analyses for specific operating conditions are of 3/16" minimum thickness and usually extend to the contact surfaces of the three body flanges for extreme service conditions.

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the measurement or control of temperatures within the limits of -100 and  $+1000^{\circ}$  F., you ought to know about these two important Taylor developments:

**1. Mercury tubing that can't tell a lie !** Imagine being able to have all the advantages of a mercury-actuated recording thermometer—on an application requiring long lengths of connecting tubing! It's long been an established fact with Taylor Accuratus Tubing. This precision-bore tubing, a Taylor invention, has a special alloy wire inside, with a coefficient of expansion so related to the tubing and the mercury that any variations in ambient temperatures along the way are counteracted on the spot. The result is *accurate* temperature recordings.

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**CALL YOUR TAYLOR FIELD ENGINEER.** These are only two of the many "plus-values" which have given

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## Flexible . . . at 70° below

THERE are very few rubber-like materials that retain their flexibility at 70° below zero. One of them is Thiokol\* synthetic rubber. In fact, "Thiokol" stocks have been compounded that remain flexible at temperatures as low as minus 85° F. And our research laboratory expects to develop stocks that will be flexible at temperatures as low as minus 100° F.

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The Thiokol Corporation laboratories have amassed much interesting test data on synthetic rubber at very low temperatures. This, added to a wealth of information on Thiokol's oil-proofness, flexibility, durability and resistance to gases under pressure, puts Thiokol Corporation in a unique position to help you with your warproduct problems. For complete technical data, write: Thiokol Corporation, Trenton, New Jersey



SYNTHETIC RUBBER "America's First"

Vol. 35, No. 1

## WHEN YOU'RE SITTING ON THE BOTTOM BATTERY PASTE

• Shown below is a complete No. 1½ Simpson Mixer unit used for compounding storage battery plate paste.



MIXERS

### SIMPSON INTENSIVE MIXERS make better battery paste faster and more economically

ANOTHER of the many war-time products that are being made better through the use of Simpson Intensive Mixers is lead oxide paste for submarine batteries. Here, where life may depend on battery paste during long hours under the sea, perfect preparation is essential and Simpson Mixers make the job easier.

Many of the leading manufacturers of all types of storage batteries are using Simpson Mixers for mixing negative and positive pastes in quantities from 50 to 5,000 lbs. per batch. They have found that Simpson Mixers provide rapid cooling, uninterrupted service...lower power consumption ... less maintenance ... and many other advantages.

Wherever there are dry solids or semisolids to be mixed, there is a Simpson unit that will handle the job better, faster and more economically. Write today for full details.

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• Wall thickness never less than specification minimum —assures full strength and loca life

long life. • Machine tool beveled ends—provide best welding surface and accurate bevel and land.

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For a pipe welding job to be right, two things must be right—the fittings and the welding. In developing WeldELLS we have kept both of these points in mind. That's why you find in WeldELLS not only everything that can contribute to the soundness of the fitting itself, but also everything that will help the welder do a job wortby of the fitting.

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January, 1943

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AN INDICATING PYROMETER THAT GIVES UNUSUAL ACCURACY IN THE PLANT

Here's a practical solution to wartime production problems of getting high-accuracy temperature information under today's speeded-up shop conditions!

Foxboro Potentiometer Indicators combine thermal precision approaching laboratory standards, with simplicity of operation that practically eliminates chances of inaccurate setting or reading by operators. Every detail is specially designed for ease and accuracy!

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Extra-large, extra-open dial of Foxboro Potentiometer Indicator enables quick, accurate setting. Built-in keyswitches for 1 to 18 thermocouple connections also add to ease of reading.

Potentiometer Instruments by HOX

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# Materials of construction destruction and reconstruction

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They make it easy to check your vacuum systems at all points, to locate leaks, to determine pressure losses in lines, to compare efficiencies of pumps and process chambers . . . to maintain systems at maximum efficiencies, thus speedingup production and obtaining desired results in drying, evaporating, impregnating, and other vacuum processing operations.

Stokes Gauges are convenient to use, either as portable instruments or on fixed mountings, in plant or laboratory. They are wide range, easily and quickly read (a few seconds only for a single reading), rugged and durable. They are carefully tested for accuracy of calibration, are widely applicable in all high vacuum processes operating within the micron and 5 mm ranges. Readings are obtainable directly, without the aid of any assisting gauge, reference vacuum, batteries or electrical connections.

Two models, one covering entire range in moderately high vacuum operations and one for very fine readings, down to a fraction of a micron. Fully described in new Bulletin 42-G.



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## CANNOT CORRODE – CANNOT LEAK

**COSTLY** shut-downs due to corroded, leaky chemical handling equipment *can* be completely eliminated by installing General Ceramics Chemical Stoneware equipment.

Chemical Stoneware's tough acid proof construction eliminates the possibility of any leakage and reduces hazards to employees and property. It is durable, too, for once installed Chemical Stoneware equipment is there for keeps – it's practical insurance against costly replacements and maintenance. Its glazed surface is easy to keep clean, to avoid contaminating products handled. The acid elevator shown here made in capacities up to 200 gallons, is only one of the many adaptations of Chemical Stoneware. Special shapes often cost very little more than standard items. Why not write General Ceramics today for a new complete bulletin?





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January, 1943

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# HELPING TO SPEED THE RUBBER PROGRAM

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Twin G-Fin Sections helped in the original experimentation on synthetic rubber in this country, and were used in the earliest American synthetic rubber plants. Today, these universal heat exchangers are widely used in synthetic rubber processes . . . and are also used throughout industry on a greater variety of heat transfer services than any other design of heat transfer apparatus on the market.

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- Used for high pressures, high temperatures, dirty liquids, and fluids of low heat conductivity.

Proved by 10 years of perform-ance and 30,000 units installed.

INDUSTRIAL AND ENGINEERING CHEMISTRY

Vol. 35, No. 1



## DATA ON DOPP-TYPE POSITIVE - SCRAPING

Basic information on heating and cooling various liquid and viscous materials, with and without Dopp-type positive-scraping, is given in our Discussion No. 3. Applications are checked on pilot plant scale as shown at the right. Resulting production economies include replacing a battery of Xanthate mixers with a single Dopp, drying in one Dopp instead of seven other units, saving 42% of the time for sulfonating, etc. As the first step toward your making savings with Dopps, let us send you Discussion No. 3.



Shows a test being made in Dopp Experimental Department where you can try a dozen different Dopp agitators operating under pressure or vacuum and at different speeds, heat with steam up to 150 lbs., cool with water or brine, etc.

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### CORROSIVE LIQUIDS



Raschig rings of Lapp Porcelain facilitate gas absorption processes by prohibiting contamination, and by standing up without crumbling under longest, most severe duty.



Lapp Chemical Porcelain Pipe is available in all standard sizes up to 8' inside diameter. Its ground ends permit installation with thin hard gaskets, eliminating at its source the chief cause of trouble in most corrosion-free pipe.

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The Lapp Valve is designed to bring liquids into contact only with porcelain. Fine grinding, polishing and lapping of bearing surfaces—and a unique spring washer arrangement—assure smooth action, and a permanently maintained seal, even under vibration and thermalchange.

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FOR TO installations for industrial-scale processing of corrosive liquids, Lapp Chemical Porcelain offers notable advantages:

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**WATER** A phone call or letter will bring a quick answer as to how Lapp Porcelain can help you meet your processing problem, quickly and with top production performance. Lapp Insulator Co., Inc., Chemical Porcelain Division, LeRoy, N. Y.

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VOI. 30, NO. 1



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