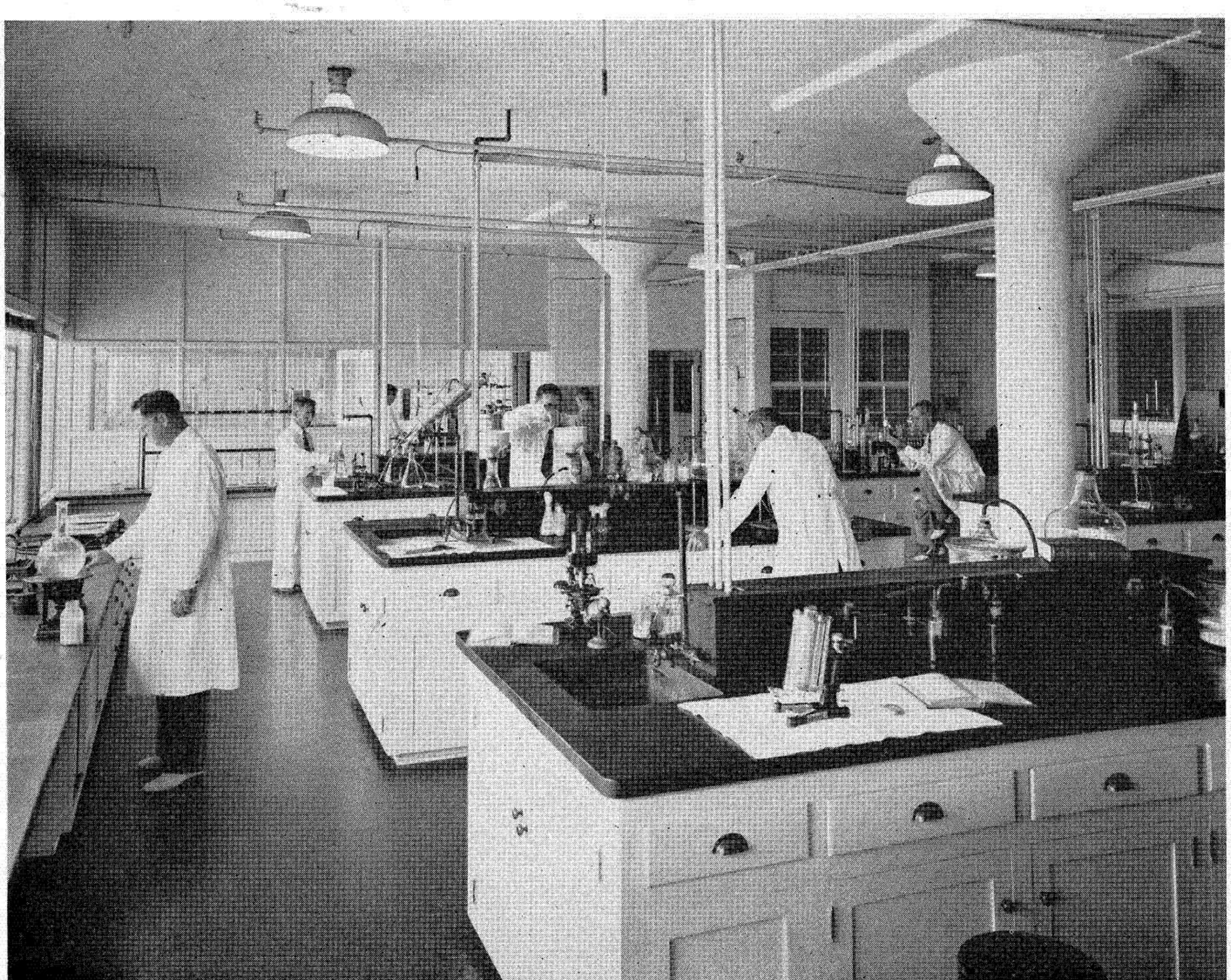
Research in the Development of

CITRUS PRODUCTS

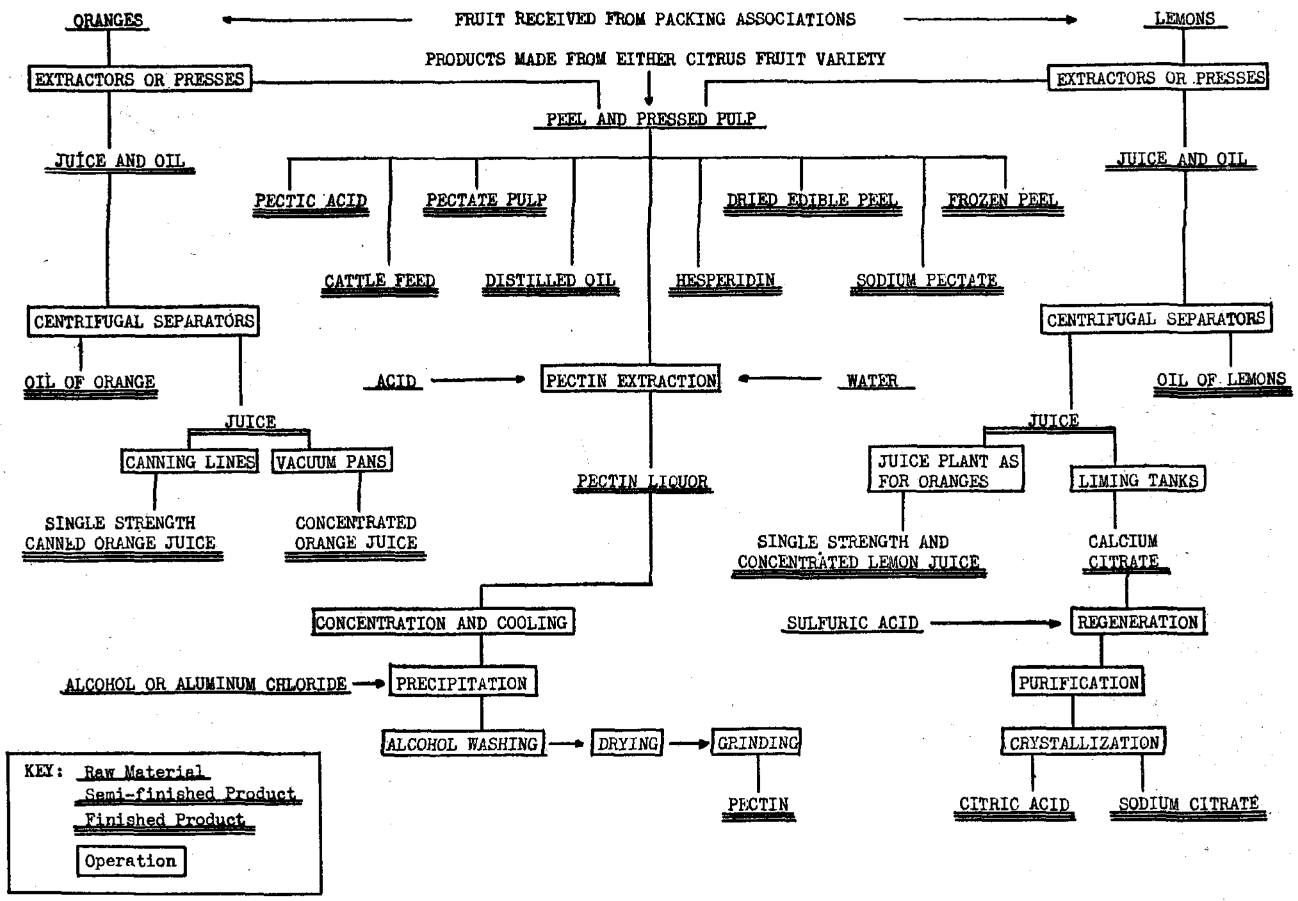
By W. E. BAIER

THE citrus products industry had its inception in Sicily some time in the early eighteenth century. It was then primarily an essential oil industry employing hand labor for expression of the oils of lemon, bergamot and orange. The years since 1900 have seen the gradual transition of citrus products to the status of a real chemical industry. Many of the major chemical developments were worked out prior to 1925, but the volume and variety of products handled have increased steadily up to the present time, with an especially marked growth coming since 1940 or just before our participation in World War II. The expansion for war production has been rapid in the states of Florida and Texas, where previously, except for canning, products development had been less active.

In this discussion we are referring to processed products of all kinds derived from oranges, lemons and grapefruit, but not including the packed fruit as prepared for the fresh fruit market. During World War I, American processed citrus products were not widely known or important to the prosecution of that war. Now, in World War II, quite a different picture is presented. The estimated gross annual value of citrus products made in the United States (still excluding fresh fruit) is about $200,000,000, and the products have been supplied almost exclusively for the three classifications: (1) Lend-Lease to the United Nations; (2) Direct use by our own armed forces; and (3) Use by processors filling Government contracts. So important are these to our war effort, the citrus products industry has at times worked under so-called "set aside orders" issued by War Food Administration, providing that a certain portion



Laboratory of the research department, California Fruit Growers Exchange, Ontario, California.



Abbreviated flow sheet of citrus products, California Fruit Growers Exchange.

(usually 20 per cent) of the entire orange crop be reserved for conversion to products to assure adequate war production.

ROMANCE OF FLAVOR

The story of the citrus products industry might be told in a number of ways, depending upon the dominant viewpoint or field of interest. The place of concentrated citrus juices in "C-vitaminizing" the infants, children and expectant and nursing mothers of war-torn England is a story in itself and a noteworthy example of socialized nutrition necessitated by an emergency.

The economic history of citrus products is equally interesting, recording as it does the several failures attending the attempts to manufacture some one product exclusively while wasting other portions of the fruit. Another possible cause of failure is the conversion by growers' organizations of their fruit into products involving relatively large and speculative purchases of outside materials. Thus the making of marmalade, which necessitates huge investments in sugar, glass and warehousing to care for the fruit normally available for processing, is usually an operation more attractive to the specialty manufacturers and merchandisers (in this case preservers) than to the primary citrus organization (such as the growers' cooperative).

Both the aforementioned nutritional and historical phases as well as others are seasoned with the flavor of romance or, more exactly, the romance of flavor; the mark of the early and continued importance of the rind essences in the world commerce of essential oils. Concerning this, it should be remembered that the study of essential oils more than any other single factor led to the methods and the training of those organic chemists who never fail to astonish with how much they can learn, analytically, with so exceedingly little, complex, and often unstable material.

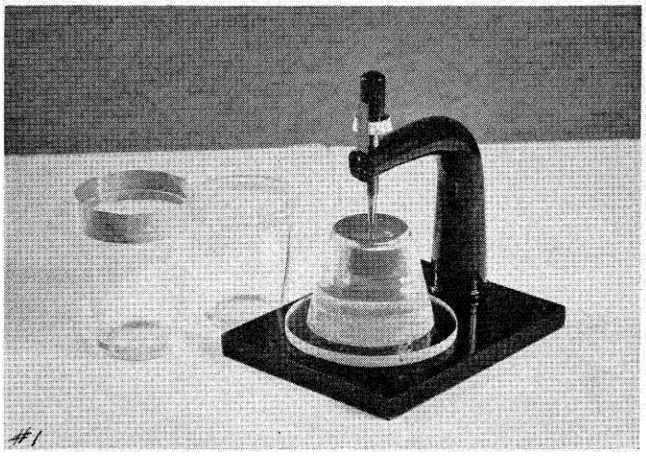
The remainder of this article has particular reference to the research activities of the California Fruit Growers Exchange, a growers' cooperative, whose early goal it was through products development to avoid the waste and the demoralizing influence on the fresh fruit market of fruit below proper standards of shipping quality.

The accompanying flow sheet will aid one in following the original as well as the improved processes of conversion of oranges and lemons.

When the more modern type of chemical research entered the industry, the classical Scheele process was (and still is) the basis for citric acid recovery. The Scheele process makes use of the insolubility of calcium citrate. The latter is precipitated from heated lemon juice by calcium hydrate and the boiling is continued to increase the particle size, thus facilitating removal by filtration. Regeneration of the citric acid, purification and crystallization follow.

Orange and lemon oils were made by a rather inefficient mechanical process. A clever continuous steam still made possible further yield of the essential oil left in the pulp, giving in this case a different type of oil, less used as a flavor but of value in perfumery. The remaining pulp was largely wasted or turned back into the soil of citrus groves as fertilizer and some was fed wet to dairy cows. The juice of lemons served as the source of citric acid, but orange juice was considered uneconomical for this purpose and was at that time without a suitable market.

Vacuum concentration of the juice yielded a product which darkened badly on storage and sometimes fermented. The earliest preservatives used were essential oils, notably clove. These, as may be supposed, were not too successful. The earliest use of concentrated juice in carbonated beverage was in filtered or clarified form because all carbonated beverages were clear, and if cloudy juice were used it would clear itself in time, the insolubles separating as an unsightly sediment. Research of chemists and bacteriologists and the efforts of others have brought about changes. Through a controlled process of high temperature flash pasteurization in stainless steel equipment, the juice is at once freed of the adverse effects of fermentive organisms and of clarifying pectic enzymes, and storage life, at reasonable temperature, has become satisfactory. The result is that, in peacetime, concentrated citrus juices are very widely distributed for local bottling of nutritious citrus beverages, both still and carbonated, especially in this country but in many other parts of the world as well.



Ridgelimeter for the determination of jelly firmness.

PECTIN

Perhaps no substance in citrus has given the research chemist more worry than pectin—that interesting material almost universally present in fruits, vegetables, fibers, etc. It must be maintained in status quo to stabilize the cloud in concentrated juices described above, because the process of enzymic or chemical degradation of pectin is used for intentional clarification of various juices. Pectin must be eliminated in the retting of flax; it is recovered in processing citrus fruit to be available for man's needs. It is used in preserving and confectionery because it forms a jelly with sugar; in the transfusion treatment of shock it is one of the most promising substitutes for human plasma and in this case it does not form a gel if it becomes cold, as does gelatin. Paradoxically, pectin is not a good adhesive, but in the form of cold water-insoluble protopectin, it is the cementing substance between the cells in the structural parts of non-woody plants. In this respect pectin is distinguished from water-soluble gums, which are the dried exudates from wounds on certain plants, and from mucilages, which are water-extracted from the seed coats of many varieties. Yet chemically and physically there are often over-lapping similarities among the pectins, gums and mucilages.

Past research perfected the production and use of pectin so that now the United Nations are getting for their annual wartime food and pharmaceutical needs approximately 2,000,000 pounds from California alone, each pound of which would make about 150 pounds of fruit jam. Incidentally, the so-called grade of a pectin is not of the quantity of jelly or jam per pound of pectin, but the pounds of sugar a pound of pectin will carry in a standard jelly of standard firmness. The jelly firmness is now precisely measured and the grade thus determined by percentage sag due to its own weight. The instrument used, shown in the accompanying photograph, is a convenient micrometer known as a Ridgelimeter, which, with a single setting, reads directly in per cent sag. Commercial powdered pectins are standardized by blending and addition of corn sugar to assure uniform performance.

The problems now receiving attention are many. Although pectin is simply carbon, hydrogen and oxygen in fairly well-known proportions, its structure is complex. A better understanding of the physics and chemistry of the pectin micelle will make possible the further improvement of special pectins for jellies low in sugar, of many useful pectic derivatives analogous to various chemical modifications of cellulose; and of pectin sols for intravenous treatment of traumatic shock.

Concerning the latter, attention has been given shock treatment, because of war needs, far beyond the dictates of any potential market return. This applies equally to manufacturers of other possibly useful blood substitutes. Because they are foreign substances, the effect of intravenous colloids, other than typed blood itself, can only be determined by experiment, first on animals and then clinically. In the case of properly prepared pectin sols, remarkably good results have been obtained with no adverse reactions or permanent accumulation, although temporary spleen involvement is sometimes observed. It is interesting that the degradation product of pectin (galacturonic acid) may not be so foreign, even parenterally administered, in view of the uronic acids found in normal animals. Glucuronic acid is usually assumed the one present in all warm-blooded animals. The possibility is now being considered, however, that in the herbivore galacturonic may comprise a substantial part of the uronic acids of the fluids and tissues. In omnivorous man, glucuronic acid may be synthesized by the body while the pectin-carrying diet (fruits and vegetables) may supply galacturonic acid. Investigators previously had shown galacturonic acid to enter into a protective detoxication process, as glucuronic acid does, but it is not known that the mechanism is the same in the two cases.

RECENT DEVELOPMENTS

The products research program of the Exchange has embraced both fundamental and practical problems. The work of past years has been directed largely toward food products. These probably will always be the most important class, especially in dollar value, considering the potential nutritional need for more widely distributed citrus juice. There is obvious merit also in the idea of striking a balance between outlets in food (including beverages and confectionery as well as feeds) vs. pharmaceutical vs. industrial channels. Recent achievements of the program, some of them the subject of continuing research, include the following items:

Food (and Feed)

1. Low ester pectin for use in low sugar jellies.
2. Improved concentrated juice products.
3. Feed (for ruminants) with enhanced nitrogen content.

Pharmaceutical

1. Pectinum N.F. VII for internal and topical medicine.
2. Hesperidin methyl chalcone, a new drug.

Industrial

1. Pectate pulp in oil well drilling mud chemicals.
2. Pectate pulp dispersion in paper coating and penicillin production.
3. Sodium ammonium pectate as a gum and agar substitute.

It is interesting to note that both possible approaches to a new product are represented in this partial list. There is the case of attempting to develop a product to meet some specific need, and the opposite case of discovering some new composition or constituent and then trying to find a field of use. Incidentally it is the writer's conviction that if a research program functions in these two ways successfully, not necessarily with equally frequent occurrence but at least occasionally, it is a test that the projects are reasonably well balanced as an

(*Continued on Page 15*)

REPRODUCTIONS OF PRINTS, DRAWINGS AND PAINTINGS OF INTEREST IN THE HISTORY OF SCIENCE AND ENGINEERING

2—Prints of Early Mechanical Road Vehicles*

By E. C. WATSON

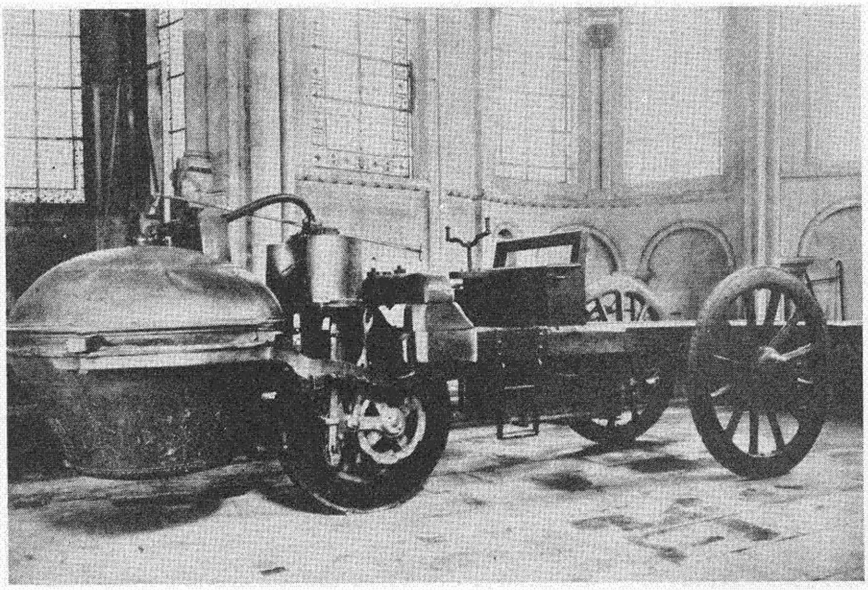


FIG. 1. Cugnot's steam tractor (1769-1770), the first practical horseless road vehicle.

THE first practical mechanical road vehicle was the steam tractor built in 1769 by Nicholas Joseph Cugnot, a French military engineer (1725-1804). It attained a speed of just over two miles per hour on a level road, but the boiler capacity was sufficient only for 12 or 15 minutes of running. By order of the French government a second tractor was constructed in 1770 for the transportation of artillery, but it was never used. It is now preserved in the Conservatoire National des Arts et Métiers in Paris, where the photograph was taken from which *Fig. 1* was made. The following description appears in the *Catalogue* of the collections in the Science Museum, London, where a small-scale model is displayed:

"It consists of a heavy timber frame supported on three wheels and carrying in front an overhanging copper boiler. The front wheel has a broad, roughened tyre, and is driven by two single-acting inverted vertical cylinders 13 in. diam. by 13 in. stroke. The two pistons are connected by a rocking beam, and their motion is transmitted to the driving axle by pawls acting on two modified and reversible ratchet wheels. The distribution of steam to the two cylinders is performed by a four-way cock actuated by a tappet motion. A seat is provided for the driver, who, by means of gearing, was able to steer the machine, the boiler and engines turning together as a fore-carriage through 15 deg. either way."

The first mechanical road vehicle to make a journey of any length was the steam carriage built in England by Sir Goldsworthy Gurney (1793-1875). The description beneath the print in *Fig. 2* reads as follows:

"The Guide or Engineer is seated in front, having a lever rod from the two guide wheels to turn & direct the Carriage & another at his right hand connecting with the main Steam Pipe by which he regulates the motion of the Vehicle—the hind part of the Coach contains the machinery for producing the Steam, on a novel & secure principle, which is conveyed by Pipes to the Cylinders beneath & by its action on the hind wheels sets the Carriage in motion—The Tank which contains about 60 Gallons of water is placed under the body of the Coach & its full length and breadth—the Chimneys are fixed at the top of the hind boot & as Coke is used for fuel, there will be no smoke while any hot or rarified air produced will be dispelled by the action of the Vehicle—At different stations on a journey the Coach receives fresh supplies of fuel & water—the full length of the Carriage is from 15 to 20 feet & its weight about 2 Tons—The rate of travelling is intended to be from 8 to 10 miles per hour—The present Steam Carriage carries 6 inside & 12 outside Passengers—the front Boot contains the Luggage."

Although planned for regular service between London and Bath, the coach of Gurney remained in an experimental state. Its chief performances were the climbing of Highgate Hill on June 14, 1828, thus demonstrating the possibilities of steam in climbing a prolonged slope, and the trip from London to Bath in 1829, the first trip of any length to be made by an automobile. Nevertheless it was not successful technically, partly because the mechanism was inaccessible and badly protected.

Between 1827 and 1838 Walter Hancock (1799-1852)

*Reprinted from *The American Physics Teacher 6*, 195 (1938) the weakest spot in the whole American educational system, namely, the lack of any sort of an apprenticeship system for providing the country with its own skilled workers rather than forcing us to import most of our skilled artisans from abroad, as we have done in the past.

I leave your imagination to fill out the picture. Great possibilities are certainly ahead. Will we have the intelligence to grasp and make the most of them? I should like to come back to this campus 20 years from today to find out.

Citrus Products

(Continued from Page 12)

industrial research program either on the so-called fundamental or the so-called practical side.

Pectate pulp is a product that resulted from research discoveries; after discovery uses had to be found for it. Sodium pectate, made by neutralizing pectic acid, has been known since 1825, as has pectin. They had similar colloidal properties, the pectic acid being perhaps less satisfactory for most purposes than the now highly successful pectin. By a simple change of process the Exchange found a pectate having much higher molecular weight which makes film-forming, viscous solutions. Moreover, it was possible to process the material without separating the cellulose, and the finished low cost material, when dispersed at the point of use, embodies both a highly colloidal sodium pectate and very finely divided cellulose.

But of what use is it? The uses are developing rapidly now, but at first considerable time was spent on some which did not materialize. One such was for quenching in heat-treating steels. Because of the low cost, controlled viscosity and non-inflammability, this appeared attractive and may yet be. However, oil well drilling mud treatment (to prevent water loss to porous strata) and paper coating (to prevent sticking of packaged synthetic rubber) have proven very much more practical than that young hopeful, the modified aqueous quenching medium.

VITAMIN P

An odd sequence of discovery occurred a few years ago regarding so-called Vitamin *P*. The Nobel Prize winner, Albert Szent-Gyorgyi, of Hungary, announced his discovery of this vitamin in lemons during 1936. Vitamin *P* was so named because it corrected excessive permeability of the capillaries and it alleviated hemorrhagic purpura. Several years earlier it had been discovered in California, in connection with spray drying of lemon juice (for cosmetic use), that an unknown constituent of the juice together with boric acid produced a brilliant yellow color. It was later found to be due to a certain group of flavones and of flavone derivatives, the same that are now considered the active materials in the Vitamin *P* substances. Here was a case of finding a color reaction for a vitamin years before the vitamin was discovered!

The research on citrus products has been accomplished in the aggregate by Government laboratories, State agencies, commercial firms, and the Exchange Research Department, which, as already stated, is the activity of a growers' cooperative and is guided by a Research Committee of grower-directors. Although the number of technically trained men employed in the Research Department has averaged about 12, and publication of results is not the objective of the work as it necessarily is in Federal and State laboratories, still the total number of publications refutes any notion that this is an industry where secrecy may have limited the progress. The present total of technical papers, bulletins and patents published is 222, covering a wide variety of subjects. It would be difficult to prophesy the future of citrus products but it can be expected to feel the influence of the same technical and scientific advancement which will guide all postwar industry.

C. I. T. NEWS

HERBERT HOOVER, JR., TRUSTEE

The California Institute of Technology announces that Herbert Hoover, Jr., has been elected to its board of trustees.

The son of Herbert Hoover and the late Lou Henry Hoover, Herbert, Jr., was born in London, England, and attended Stanford University, graduating in 1925 with a B.A. degree. In 1929 he won his M.B.A. degree at Harvard University. He was a member of the research staff of the Harvard Business School in 1928 and 1929, and from 1929 to 1931 he was communications engineer for the Western Air Express, followed by three years of service in the same position with Transcontinental and Western Air, Inc. In 1934 and 1935 Mr. Hoover was a Teaching Fellow at the California Institute of Technology.

Mr. Hoover is president of the Consolidated Engineering Corporation and the United Geophysical Company, both with offices in Pasadena, Calif. He is president of the United Engineering Company of New York and a director of the C. R. B. Educational Foundation. He also is a member of various professional societies, including the American Institute of Mining and Metallurgical Engineers, the Institute of Radio Engineers, and the Society of Exploration Geophysicists.

Mr. Hoover, a resident of San Marino, Calif., is married and has three children, Margaret Ann, Herbert, III, and Joan Leslie.

CHINA IN PEACE AND WAR
As related by E. Harrison King

THE alumni dinner meeting held at the Hotel Clark on the evening of March 8 had as its speaker E. Harrison King, instructor in hydraulics at the Institute. Mr. King vividly described China as he knew it while professor of civil engineering at St. John's University near Shanghai and as an internee in a Japanese internment camp following America's entry into the war in 1941.

Mr. King first told of the general Chinese background by comparing Chinese cities with Chicago, New York, and other American cities. The skyscrapers of Shanghai are high and numerous, reminding one of New York City. At the other extreme of comparison, Mr. King spoke of one city of 130,000 population near Shanghai which has no railroad or highway leading to or from it. The city has a wall and moat surrounding it, the moat joining with canals which permit small sailboats to reach the outskirts of the city. The only other means of transportation into the city is by cart and dirt path.

Mr. King commented that a few of the customs and methods of the Chinese are not understood and therefore not respected by many Americans. However, he stated, if these customs and methods were understood they would be recognized as effective and respectable. Mr. King explained that the attitude of the Chinese is that they can work their problems out in their own way