These results show very definitely that very little change is effected during the distilling operation, as for example, the iodine numbers on all of these fatty acids is practically the same in the original fatty acids as in the distillate, with the sole exception in the case of Tung Oil, where there has been a definite change. The remarkable thing in this table is the fact that an oil like Perilla Oil with an iodine number of 198.0 has been successfully distilled without any appreciable change, and with a final yield of 90.8 per cent. It also is noted that the color of the distillate in all these cases is very remarkable. In the distillation of linseed fatty acids and Tung Oil fatty acids, apparently the flash method of distillation does not cause any change in these fatty acids so that it is possible to commercially distill these fatty acids in a satisfactory manner and this has been done on a large scale.

Aside from the large practical plant units, there is precisely similar practical small scale apparatus, with a capacity of approximately 50 gallons per day, which is available for tests on any material of a fatty acid nature, either animal or vegetable, in which anyone may have a special interest. In this manner definite data can be economically obtained on any class of fatty acid with a production of distillate in sufficient quantity to accurately indicate the possibilities in respect to finished distillate yields and distillate quality characteristics.

A NEW PRINCIPLE AND AGENT IN DETERGENT OPERATIONS

The Utility of Sodium Hexametaphosphate as an Adjuvant to Soap*

By BERNARD H. GILMORE**

The story of the technical development of sodium hexametaphosphate from a laboratory curiosity to a commercial product is one of the romances of modern industrial science. The commercial use of sodium hexametaphosphate in the soluble, glassy form is a research creation of Hall Laboratories, Inc., Pittsburgh. The epochal research of R. E. Hall and his collaborators at the Bureau of Mines, which culminated in the establishment of a system of internal treatment of boiler feed-waters that was based upon the maintenance of the proper chemical equilibria at heating surfaces, marked a new era in conditioning methods. However, in the early days, a most serious obstacle to the successful application of the system proposed by Hall was the problem of deposits in the feed-lines. While the orthophosphates of sodium were found to be the most suitable reagents for precipitating calcium and magnesium as nonadherent sludge in boilers operated at moderate and high steam pressures, the insolubility of calcium phosphate which adapts them for this purpose was responsible for feed-line scale. This shortcoming of the orthophosphates led to an intensive investigation of the properties of all the known alkali metal phosphates. The successful termination of this search for a substitute for the orthophosphates led Hall and Jackson to propose the use of the meta and pyrophosphates for boiler-water softening. But before the discovery that the proper use of sodium metaphosphate eliminated feed-line scale could be utilized, it was necessary to establish commercial production of the chemical. Until October, 1929, a soluble sodium metaphosphate was not available in commercial quantities at any price, either here or abroad. With use once established, however, there was developed a commercially successful process of manufacture that combined the thermic production of the orthophosphate and its conversion into the metaphosphate form in a gas-fired furnace. Large quantities of this unusual and useful chemical are now being produced annually, and are being marketed by Calgon, Inc., of Pittsburgh.

BERNARD H. GILMORE

Properties of Sodium Hexametaphosphate

If mono-sodium phosphate is heated, water of crystallization is first expelled; anhydrous monosodium phosphate on further heating first yields acid sodium pyrophosphate:

$$2NaH_2PO_4 \overset{\Delta}{>} Na_2H_2P_2O_7 + H_2O \uparrow$$

Sodium acid pyrophosphate is stable and crystallizable, and has in aqueous solution a pH value of about 4.5. Its chief use is as the acidic constituent of baking powder. On further heating at low temperature, it forms sodium metaphosphate:

$$Na_2H_2P_2O_7 \overset{\Delta}{>} 2(NaPO_3) + H_2O \uparrow$$

The sodium metaphosphate thus formed is but poorly soluble and is supposed to be either monometaphosphate or a highly polymerized form. If the insoluble metaphosphate is heated to redness, it melts. After chilling the molten mass, a highly soluble glass-like product results. It is believed that this is sodium hexametaphosphate $(NaPO_3)_6$. This is the soluble metaphosphate ("Calgon") with which this paper will deal.

While the solubility of sodium hexametaphosphate is not definitely known, solutions of it containing 70 per cent. by weight of solute have been made. In aqueous solution sodium hexametaphosphate rehydrates to form the mono-sodium orthophosphate. This reaction is accelerated in the presence of both acids and alkalies. As it is used more frequently in alkaline solution, the rate of reversion at relatively high pH is of greater industrial interest and importance. High temperatures, high concentrations, high pH values, and the presence of calcium and magnesium all increase the rate of reversion. A concentrated (25 per cent.) solution at normal room temperatures and at its characteristic pH value reverts about 10 per cent. per month, an unimportant amount. A 2 per cent. solution at boiling temperatures, at a maintained

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pH value of 9.6 and in the presence of calcium, reverts to the extent of 33 per cent. in 5 hours.

The pH value of pure sodium hexametaphosphate in dilute solution (¼ to 1 per cent.) is in the neighborhood of 5.5. The commercial product in so-called "unadjusted" form and in solutions of similar concentration has a pH value of 6.8 to 7.0. The higher pH value is due to the presence of about 10 per cent. of sodium pyrophosphate. For its use in conjunction with soap, an addition of 4 per cent. soda ash and 2 per cent. sodium bicarbonate in briquet form is made to the dry metaphosphate, so that the pH value of the ¼ per cent. solution becames about 8.5.

The most notable characteristics of sodium hexametaphosphate are its water-softening action and its solvent action on insoluble compounds of calcium and magnesium. Reduced to its simplest terms, water-softening refers to reducing the concentration of calcium and magnesium ions of a given water. The conventional industrial methods for softening water are based either upon (1) precipitation or (2) base exchange; both depend upon actually removing calcium and magnesium from the water.

Precipitation methods depend upon converting the soluble calcium and magnesium compounds into insoluble forms, whereby they are precipitated from solution, as the carbonate in the case of calcium and as the hydroxide in the case of magnesium. The degree of softening obtained by this method is conditioned by the completeness of the equilibria involved as well as by the solubility of the end products. The practical limit of residual hardness for softening in the cold is about 50 parts per million of calcium carbonate and for the hot process it is about 25 parts per million.

The base-exchange or zeolite process is based upon an exchange of sodium ions for calcium and magnesium ions. While this exchange is not complete, the equilibria value is very low. It is unfortunate in this connection that the term "zero" hardness" has been coined, because it signifies a zero soap test, whereas zeolite-softened water usually contains some calcium and magnesium even when the apparatus is operated at maximum efficiency. A well operated zeolite softener will deliver a water ranging between 5 and 15 parts per million of calcium carbonate during its softening period.

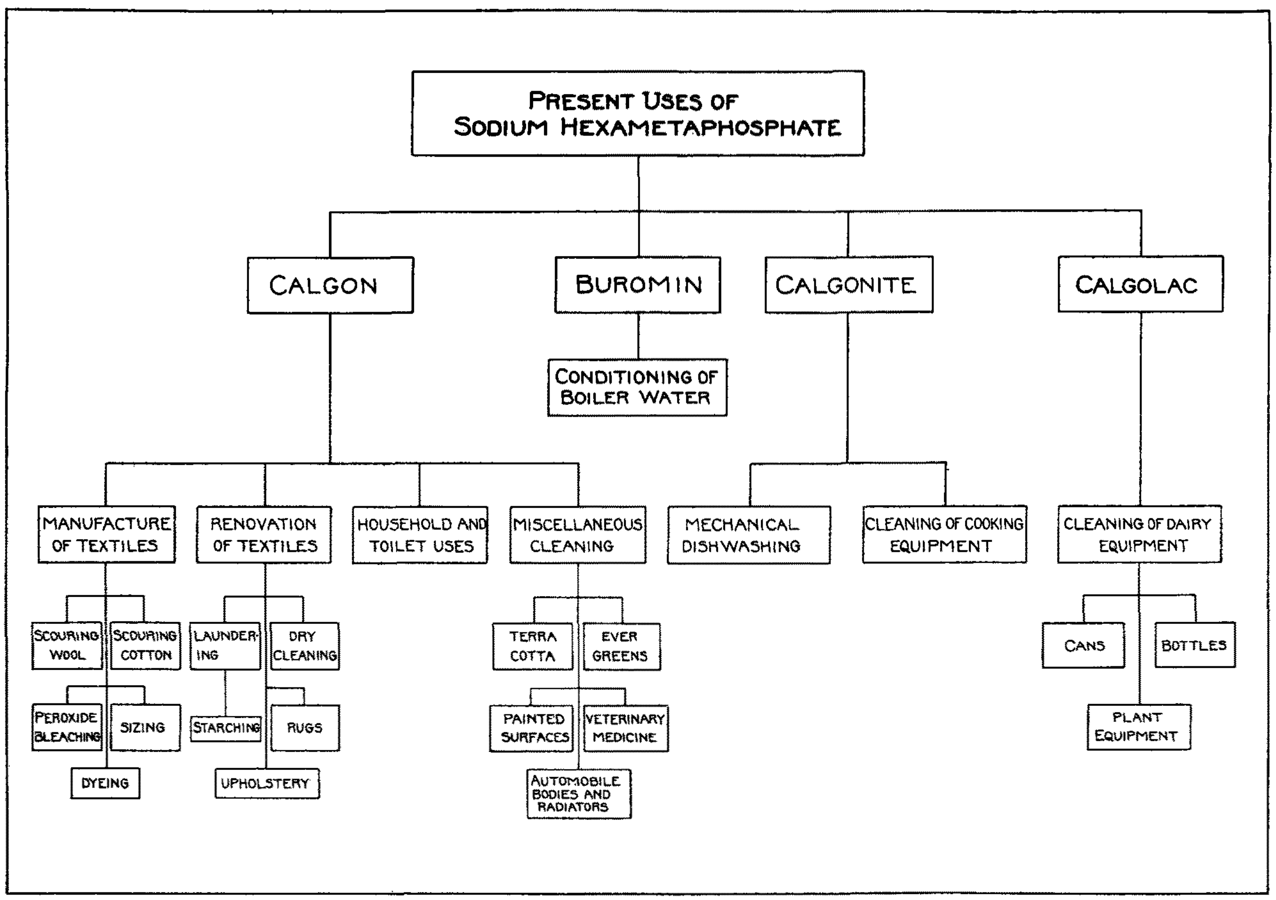
In neither case is the water so free of hardness that the precipitation of metallic soaps will not occur. This is due to the great insolubility of calcium and magnesium soaps.

With the commercial advent of sodium hexametaphosphate a new process of water softening has been introduced. This process, which has been named "sequestration" by its inventor, R. E. Hall, is unique in that it does not involve the precipitation or removal of calcium and magnesium from the water. It involves rather, the suppression of the ionization of calcium and magnesium by the addition of the appropriate amount of sodium hexametaphosphate. The avidity of sodium hexametaphosphate for the ions of calcium and magnesium is so great that in effect they become non-existent in the presence of it. If an appropriate amount of sodium hexametaphosphate is added to a water containing determinable quantities of calcium in solution, there is no resultant change in appearance of the water. If now this solution is tested by different reagents capable of precipitating calcium, for example, sodium carbonate, sodium oxalate, sodium orthophosphate, and finally soap, a negative result will be obtained. The conclusion to be drawn from these experiences is that while calcium may be present calcium ion is not. The same behavior is characteristic of magnesium.

Alkaline solutions of sodium hexametaphosphate also possess the property of dissolving the insoluble compounds of calcium and magnesium, notably the carbonates, the phosphates, the oxalates, and the soaps. The demonstration of the solvent action of the metaphosphates toward "lime soaps" presents a very spectacular and convincing experiment, because it is accompanied by a very vigorous lathering or sudsing by the regenerated soap.

This solvent property towards insoluble compounds is a characteristic of complex-forming substances and indeed there is every reason to believe that the mechanism of the water-softening action of sodium hexametaphosphate is one of complex formation. The soluble complex ion involved has a very low order of ionization—so low in fact that it is impossible to satisfy the solubility product of any of the known insoluble compounds of calcium and magnesium in the presence of excess sodium hexametaphosphate.

The applicability of such an agent as sodium hexametaphosphate to a detergent process should be immediately obvious. Neglecting for the moment any specific detergent property of the metaphosphate, a once hard water which contained an excess of sodium hexametaphosphate over the softening requirement would be a superior medium or vehicle for cleaning



processes to distilled water. It would be capable of dissolving calcium and magnesium deposits as well as protecting the detergent agent from calcium and magnesium ions encountered in cleaning. Such a water may be spoken of as having a negative hardness. Or if distilled water is considered to be of zero hardness on the basis of its freedom from calcium and magnesium, a concentrated solution of sodium hexametaphosphate might be regarded as having a hardness of zero Absolute, as compared to zero Centigrade.

Specific Detergent Action of Sodium Hexametaphosphate

Aside from the unique advantages of sodium hexametaphosphate as a water softening agent, it has demonstrated specific detergent properties of interest. One of the earliest instances of this behavior occurred in connection with the problem of cleaning elevator cable. In one of the modern office buildings in Pittsburgh which had installed high-speed elevators of the self-aligning type, considerable difficulty was experienced in spotting the cars correctly at the floor levels. This difficulty was traced to slippage of the elevator cable, which in turn was caused by the presence of a film of grease on the surface of the cable. This grease originated in the hemp core of the cable where it had been employed as a lubricant to increase pliability. The deposit of grease was easily removed by scrubbing the cable with a dilute solution of sodium hexametaphosphate. A further instance of the specific detergent action of sodium hexametaphosphate was seen during a study of its laundering properties. It was found that greasy wiping rags and mechanics' overalls which were heavily soiled could be washed satisfactorily with a dilute solution of sodium hexametaphosphate, to the exclusion of soap or alkali.

Because of its neutral character as well as its detergent action, sodium hexametaphosphate has proved of great utility for the cleaning of painted surfaces including woodwork and walls. One manufacturer of a painted textile wall covering has also produced a cleaner for its material which contains a large proportion of sodium hexametaphosphate.

During the construction of the new Mellon Institute building, considerable difficulty was experienced in cleaning the glazed terra-cotta walls of the interior courts with a strongly alkaline detergent. The use of sodium hexametaphosphate for the purpose led to superior and more rapid cleaning with a minimum of discomfort to the workers.

Use of Sodium Hexametaphosphate as an Adjuvant to Un-Saponaceous Cleaning Agents

The washing of utensils and dishes in automatic equipment constitutes a type of detergent process in which the use of sodium hexametaphosphate is singularly advantageous. A recent paper by Schwartz and Gilmore entitled "Sodium Metaphosphate in Mechanical Dishwashing" discussed the utility of this agent in this kind of cleaning process. According to present day practice even when dishes are rinsed at a sufficiently high temperature to insure rapid spontaneous drying, wiping and polishing are ordinarily necessary to avoid "lime stains." This discoloration is due to the formation of films of insoluble compounds which result from interaction between the cleaning agent, the mineral salts in the water, and the soil on the articles being washed. Heretofore, the formation of such insoluble deposits has been unavoidable because the alkaline salts which are commonly considered to be the best detergents, namely, sodium metasilicate and trisodium phosphate, form very insoluble compounds with the alkaline-earth metals present in the average water supply. Thus it was shown that even when no soil was present, insoluble films were built up on china and glassware washed with the best commercial dish washing compound available, when wiping was not resorted to between washings.

While sodium hexametaphosphate lacks the powerful saponifying action towards fats and the solvent action toward proteins of the more alkaline detergent salts as exemplified by trisodium phosphate and sodium metasilicate, its admixture with these salts leads invariably to generally improved results. This enhanced detergent efficiency has been attained by keeping the precipitation factor at a minimum. Thus the function of sodium hexametaphosphate has been to prevent the precipitation of the insoluble compounds of calcium and magnesium during the washing and rinsing processes.

Numerous practical advantages accompany the use of sodium hexametaphosphate as an ingredient of dishwashing compound. Because it eliminates the formation of insoluble films it does away with the necessity for wiping and polishing glassware. It also removes the necessity for soaking and scouring chinaware. A further advantage is that it no longer necessitates deliming and cleaning the washing machine with acid, a practice which is periodically necessary when a detergent not containing sodium hexametaphosphate is employed.

In detergent compositions for the cleaning of dairy equipment, the incorporation of sodium hexametaphosphate has been particularly effective, as formerly such compounds were subject to the same shortcomings as the ordinary dishwashing compounds, namely, the incomplete removal of soil owing to precipitation during rinsing. Milk cans washed with metaphosphate compositions have been notably clean and free from odor. A particularly troublesome phase of dairy cleaning is the removal of milk stone, an incrustation which forms upon heating surfaces. Milk stone is not of uniform composition, but has been found to be composed of protein, fat, and the inorganic constituents, calcium, magnesium, sodium, iron and phosphorus. Milkstone tends to trap precipitates made by interaction between alkaline cleaners and hard water forming adherent deposits which are very difficult to remove either by mechanical or chemical means. The daily use of an alkaline cleaner containing sodium hexametaphosphate has led to the elimination of milkstone as a cleaning problem in the plant of a large food manufacturer where milkstone occurred as a deposit in pipe lines and cooking vessels in which cream soups were prepared.

Sodium hexametaphosphate has also been found useful in the cleaning and the protection of instruments and equipment, particularly metal articles in dental and medical offices and clinics.*

Use of Sodium Hexametaphosphate With Soap

To date, the most successful industrial application of sodium hexametaphosphate has been in commercial laundering. A joint investigation** of the Buromin Company of Pittsburgh, Mellon Institute, and the American Institute of Laundering developed the fact that sodium hexametaphosphate possessed distinct utility in laundering processes. At the outset the laundry industry did not appear to offer a very promising field for the introduction of sodium hexametaphosphate because of the fact that nearly all commercial laundries with the exception of many hotel and institutional laundries practiced water-softening—usually by the zeolite process. However, the demonstration of the fact that appreciable amounts of lime soaps accumulated in laundry work that was washed in zeolite-softened water seemed to point out a genuine function for sodium hexametaphosphate in commercial laundering processes.

Lime soaps—the insoluble bodies resulting from the action of hard water on soap—are objectionable from two viewpoints. First, their presence is indicative of a soap waste that is actually an economic loss. More important is the fact that they are prejudicial to the "quality" of the finished laundry work, because they not only discolor fabrics, but they also make it increasingly difficult to clean them because of the water-repellant property of the lime soaps. The disadvantages and objectionable features pertaining to lime soaps have been recognized for many years by progressive laundryowners.

Sodium hexametaphosphate was introduced into the laundering process as an agent for the improvement of laundering methods by providing for the solution and removal of lime soaps as an integral part of the washing process. While its use enables the elimination of some soap by its regenerative action on the inactive lime soaps, any tendency to regard sodium hexametaphosphate as a substitute for soap or to attempt to justify its usage on a basis of soap economy has been discouraged, and its unique character as an aid to improved color has been emphasized.

The research also demonstrated that sodium hexametaphosphate was harmless to all textile fabrics and to colors, so that it can be used with safety and advantage in washing all classifications of laundry work.

The fact that sodium hexametaphosphate is filling a needful role in the process of laundering is attested by the number of laundries—more than seven hundred—which use it regularly.

Related to the laundering usage of sodium hexametaphosphate is its extensive application to the "wet cleaning" processes practiced in the dry-cleaning industry. It is also widely used in the cleaning of rugs and upholstery fabrics, where its neutral character, together with its water-softening and solvent action, is of particular advantage.

Sodium hexametaphosphate has found diverse applications in the textile industry. It is being used in the kier-boiling of cotton; it has been used to advantage in the scouring of lime-pulled wool. Its use in wool-scouring has led to cleaner wool which is characterized by better behavior during finishing. Its use in the dye bath permits better penetration and more level dyeing. Wool scoured with the addition of sodium hexametaphosphate has a better handle. This is particularly true of piece-scoured goods.

*A full report on this work will soon be published by Dr. A. Koenig, one of my coworkers.

**A full report of this work, entitled "The Application of Calgon in Laundering," was published in the Starchroom Laundry Journal, P. 24, October, 1933.

A novel use* for sodium hexametaphosphate has been in connection with the washing of evergreens coated with a tarry film of combustion products. The use of a dilute solution of sodium hexametaphosphate together with a small amount of soap softened the tenacious film so that it could be easily removed by mechanical means.

In the practice of veterinary medicine** the use of a solution of hexametaphosphate has been found to be of decided advantage in cleaning the skin and fur of animals that have been treated locally with ointments. Its use in the grooming of dogs for show purposes has also been accompanied with very favorable results.

The Present Status of Sodium Hexametaphosphate in Detergent Processes

What is the present status of sodium hexametaphosphate in industrial detergent processes? The tendency among those who are actually engaged in the study of its possibilities in this field is to subordinate its own specific application as a cleaning agent to its broader application as an adjuvant in every conceivable type of cleaning process conducted in hard water. The term adjuvant, regardless of the detergent used, connotes the idea of supplementing or facilitating action. The fact that water is almost universally used as the vehicle or medium in conducting cleaning processes, and the fact that the alkaline salts and soaps commonly used as cleaning agents are incompatible with hardness in water, serve to indicate the utility of a sequestering agent, such as sodium hexametaphosphate, in cleaning processes. Its use enables a new conception of cleanliness, because by suppressing the offending calcium and magnesium ions, it facilitates the complete removal during rinsing of dirt and detergent alike without leaving a residue on the articles being washed.

The alternative to conditioning the water to suit the detergent is to condition the detergent to suit the water. This approach to the hard water problem has proved very successful in Germany and has led to the development of some interesting new detergents, among them the Igepons and the higher fatty alcohol sulfates. The rights to the manufacture of the latter class of compounds and to their distribution in the textile field were acquired by a leading producer of synthetic chemicals, while exclusive rights in the soap field were granted to a leading soap manufacturer. Speculation has since been rife as to the effect of these new agents on the future of soap. The principal advantage of the sulfated fatty alcohols is their good resistance to hard water, as their calcium and magnesium salts are soluble and effective; however, these agents do not possess the power of dissolving insoluble calcium and magnesium deposits which may constitute a portion of the soil. Supplementary advantages are their neutral character and freedom from hydrolysis, and their resistance to acids because the free acids are soluble in water and surface-active.

The principal shortcoming of soap as a detergent is its sensitivity to hardness. It is the firm conviction of the speaker that the use of sodium hexametaphosphate as an adjuvant to soap will at least place soap on a parity with the fatty alcohol sulfates insofar as detergent processes conducted in hard water are concerned, because the combination will possess a solvent action on existing deposits of lime soaps and other insoluble alkaline-earth compounds that is not a characteristic of the newer detergents. It is his further conviction that the usefulness of these compounds will be limited to the specific processes in which their neutrality and their stability to acids particularly adapt them.

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*A more detailed description of this application may be found in The American Home, p. 52, December 1933.

**See "A New Veterinary Cleaning Agent," Veterinary Medicine, vol. 29, No. 1, January, 1934.

MANCHURIAN SOYBEAN SURPLUS REPORTED SMALLER

The 1934-35 export surplus of soybeans in Manchuria, the world's largest producer and exporter of this product, has been officially estimated at 3,065,000 short tons, a reduction of approximatey 24 per cent, compared with the 1933-34 surplus, and a reduction of about 31 per cent compared with the average surplus for the past five years, according to a report to the Bureau of Agricultural Economics from Assistant Agricultural Commissioner F. J. Rossiter at Shanghai.

The United States is particularly interested in the Manchurian soybean situation this year because of the extreme shortage of all high protein feeds resulting from the drought last spring and summer. This country has always been an importer of soybean cake and meal from Manchuria and there is more need this year than for many years for imported supplementary protein feedstuffs, says the Bureau. The drought also seriously reduced feed crops in Europe so that the reduction in the Manchurian soybean surplus will also be of special concern to European livestock industries this year.

The 1934-35 soybean crop in Manchuria has been officially estimated at 3,968,000 short tons compared with 5,072,000 short tons in 1933-34 and with the average crop of 5,346,000 short tons for the five years ending 1933-34.

While the crop was officially estimated at only 3,968,000 short tons Rossiter is of the opinion that it amounted to about 4,400,000 short tons. Even at this higher estimate the 1934-35 crop would be the lowest in more than ten years.

The smaller harvest this year is due to a reduction of 6 per cent in the acreage and to low yields resulting from excessive rain and floods last July and August, says Rossiter. Among the factors accounting for the acreage reduction this year are shifts to other crops because of low prices during 1933-34, abandonment of farming in favor of construction work, and reduced emigration from China to Manchuria.

The Manchurian export surplus of soybeans moves to world markets mainly in the form of soybeans and soybean cake and meal. Soybean oil exports are relatively small. The carryover of soybeans on hand from the 1933-34 crop on October 1, 1934, amounted to 200,000 short tons. Adding this to the estimated 1934-35 crop of 3,968,000 short tons gave a total supply of 4,168,000 short tons. Deducting 1,103,000 short tons for home consumption and seed leaves only 3,065,000 short tons available for export. The exportable surplus for 1933-34 was 4,020,000 short tons compared with the average of 4,438,000 short tons for the five years ending 1933-34.

The export demand for Manchurian soybeans as beans comes largely from Germany, the Netherlands, Denmark, and England. Of the total exports of 2,625,000 short tons of beans in 1933-34 the European market took 75 per cent and Japan 20 per cent. Europe is expected to purchase all available beans this season because of the feedstuff shortage in Central Europe, says Rossiter. The demand from Japan, however, is expected to show a decline. Dairen dealers are also hopeful of increasing sales this year in South China.

The export demand for Manchurian soybean cake and meal in the past has depended mainly upon Japan and China where this article is used extensively as a fertilizer. Exports in 1933-34 amounted to 1,123,000 short tons, of which 85 per cent went to Japan and 10 per cent to China. Shipments to these markets are expected to show a decline in 1934-35. It is believed, however, that exports to the United States will be considerably larger than last year when they amounted to 24,699 short tons. Exports to the United States thus far this season have been considerably above those for the corresponding period last year.

Manchurian exports of soybean oil have been declining steadily in recent years and in 1933-34 amounted to only 72,000 short tons, the lowest in 15 years. Chinese and European markets usually take practically all of the shipments. Purchases by China last season, however, were very low, amounting to only 18,000 short tons or 25 per cent of the total, while Europe, after several years of declining imports, took 53,000 short tons or 73 per cent of the total. Europe has found it profitable since the war to crush her own soybeans and for that reason has been reducing her imports of Manchurian oil and oil cake. The United States in 1933-34 took only 760 short tons of Manchurian soybean oil compared with 2,000 short tons in 1932-33.

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Appointed Representative

The formation of Schimmel & Co., Inc., manufacturers and dealers in essential oils, aromatic chemicals, perfume raw materials and flavors, has recently been announced. Office and laboratories are located at 601 West 26th Street, New York City. As of January 1, 1935, this company was appointed the representative in the United States and Canada for Schimmel & Co., A. G., of Miltitz-Bei-Leipzig.