Refining of Drying Oils

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REFINING, as practiced by the drying oil industry in this country today, is relative both in connotation and application. Webster defines the term as "to make pure or purer." Obviously the degree of purity as produced by refining is subject to many variations which will be enumerated later.


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Whereas refining in the edible oil industry is concerned mainly with producing an oil stable towards oxidation, the direct opposite is true in the drying oil industry. We are primarily interested in improvement of the oil in the direction of unstability to oxidation, or faster and better drying. The degree of refining of drying oils is determined to a large extent by the following factors: a) quality of crude stock, b) customer specifications, c) industry specifications, d) federal, A.S.T.M., and Armed Services specifications, e) uses of refined oils, f) technical knowledge of refiner, g) equipment, and h) economics.

From the above it is obvious that a great many refining procedures must be used in order to produce oils having the necessary and desirable characteristics. It is in the interest of both the refiner and the user that the most suitable process, considering above factors, be employed. In general, it should be emphasized that the optimum procedure in all cases is one involving the least amount of work to accomplish the desired results. The cost of refining and the technical difficulties will be reduced in direct proportion to the simplicity of the refining procedure. The oils to be considered at this time, representing the most important materials in the protective coatings field, are a) linseed, b) fish, c) tung and oiticica, d) soya, e) safflower, and f) miscellaneous, such as tall oil. Since linseed is the predominant raw material, this paper will be concerned mainly with its refining. Soya is included since it is rapidly gaining importance in the field through its suitability to further processing, increasing its utility.

Refining Methods

The refining of drying oils on a commercial basis is accomplished at the present time by one or several of the following methods: a) hydration, b) alkali refining, c) acid refining, d) solvent segregation, and e) miscellaneous.

Hydration is the term applied to treatment of crude stock with water, in any of its phases, alone or as very dilute inorganic salt solutions. In general, the industry refers to this process as clarification or degumming.

Alkali refining refers to any method of treatment of crude or degummed stock with alkaline solutions. The usual chemical agents employed are caustic soda, soda ash, sodium silicate, lime, etc. These are used separately or in combination depending upon procedure and desired results.

Acid refining is accomplished mainly through the use of sulfuric, hydrochloric, and phosphoric acids as well as acid salt solutions such as zinc chloride, monosodium phosphate, etc.

Solvent refining is relatively new in the industry. One system has been in operation on soya and linseed for several years while another was recently applied to fish oil refining.

In a rationalization of the problem of refining, basic and fundamental knowledge of the properties of the oils and treating agents is absolutely essential. In the oils we are concerned with a) fatty acid glycerides, b) free fatty acids, c) foots which consist of phospholipids, gums, and proteins, and oil-soluble materials, d) color bodies, and e) waxes or stearine.

As a rule, the fatty acid glycerides are not affected by the refining processes. These are mainly involved in the further processing of the refined oil, such as oxidations, polymerization, etc. The problem of refining is then resolved into the determination of a procedure which will alter the character of the crude stock with respect to the above components in such manner as to produce the desired grade of refined oil at the lowest cost.

Hydration

Most commercial seed oils contain varying amounts of foots or gums in the crude state as a result of the crushing or extraction of the seed. These materials may be phospholipids such as lecithin, vegetable gums and resins, colloidal proteins, and oil soluble organic matter. Inasmuch as they are non-drying constituents and often exhibit anti-oxidant effects, it is essential that they be effectively removed. Where this is to be done without altering the general character of the oil with respect to color, acidity, etc., the process of hydration is employed.

Thurman (1) discloses methods for removal of phosphatides from vegetable oils by continuous methods. Parkins and Walker (2) winterize and degum linseed oil simultaneously. Bailey (3) covers this subject thoroughly with reference to soy-bean oil. Equipment manufacturers (4) have developed complete batch and continuous systems for hydration of various oils.

As a practical approach to the problem of degumming we have made a study of the physical and chemical behavior of the foots in linseed oil. From a physical viewpoint it has been definitely established that this material is hydrophilic in character and has a tendency to bind water within very specific limits. It has also been determined that its specific gravity is greater than that of the oil, as demonstrated by its settling tendency upon long standing.

Its chemical properties show solubility in dilute salt solutions. In addition to this, sulfuric acid has a strong dehydrating and charring effect on this material with the formation of a heavy black residue.

Utilizing the above information, it is fairly easy to establish the optimum procedure for producing a foots-free linseed oil. Since the hydrophilic character of the foots has been demonstrated, it follows that treatment of the oil with the proper amount of water to hydrate the material will further increase the specific gravity and form a heavy sludge which can be easily separated. However, it is necessary that a proper balance be established between water used and foots present to facilitate separation.

The proper amount of water to be used can be determined by specific gravity measurements of the crude oil. Experimental data have shown the following results for specific gravity versus foots content in linseed oil:

Specific Gravity		Foots	
Crude linseed oil	.9340	Maximum	2% by wt.
Degummed linseed oil	.9315	Less than	.2% by wt.

All types of oil regardless of production methods fall within this range of specific gravity. This fact thus allows the use of specific gravity determinations to classify the oil for the purpose of determining proper amount of water for degumming.

The use of water in an amount equal to the percentage of foots present as indicated by specific gravity measurements assures adequate hydration for purposes of separation. Insufficient water necessary to bind the foots or gums simply means incomplete removal while excess water will tend towards a watery condition. The latter also favors a 2-layer throw-out since the water-in-foots emulsion cannot be diluted with the inner phase. Consequently some difficulty in separation occurs in this case with a corresponding loss in yield of degummed oil.

With the utilizing of the above information continuous or batch methods may be designed depending upon equipment available and capacity of production desired. Temperatures of oil ranging from 90°F. to 140°F. may be used. In general, higher temperatures

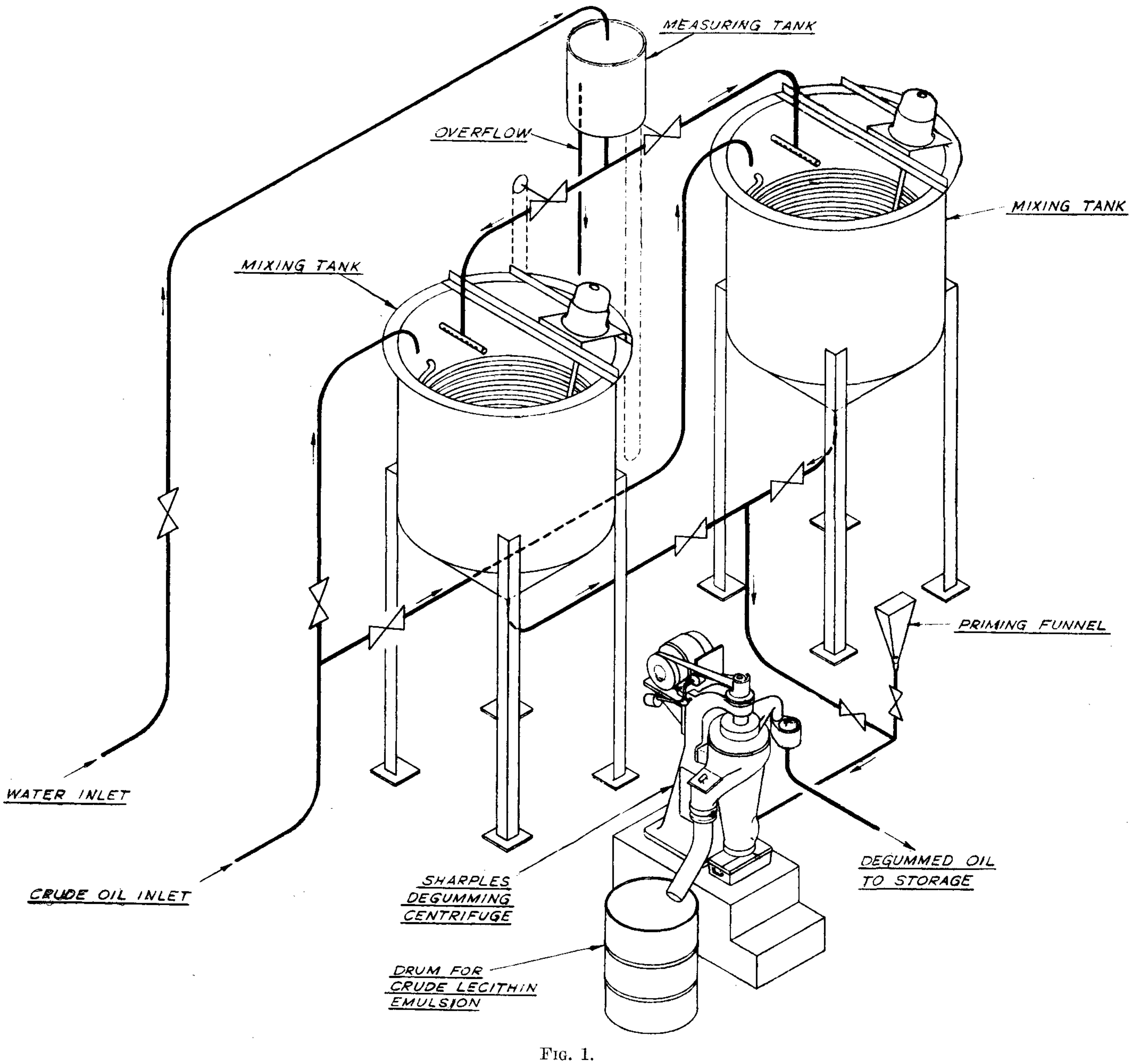

FIG. 1.

reduce the viscosity of the oil allowing faster and more efficient separation of the gum emulsion.

The flow diagram for the hydration process is very simple as illustrated in Figure 1. In the continuous method oil and water are metered to a mixing chamber where the emulsion is formed. This is then passed continuously to high speed centrifuges where the separation is performed. In the batch method a suitable cone-bottom tank equipped with adequate agitation and heating coils is needed. Water is sprayed over the surface of the oil while agitated, and this is continued for a short period after addition of total water. The agitation is then stopped and the batch allowed to settle 12-24 hours. The degummed oil may then be drawn off the compact foots layer on the bottom and dried by filtering or through use of a vacuum tank. The foots can be drawn off the bottom or washed out for further treatment.

Where steam is employed, the same procedure is followed except that it is introduced under the surface of the oil. The oil acts as a condensing medium for the steam; the condensate immediately emulsifies the foots. Separation is effected as before.

In soybean oil, the same general procedure is followed. Here the foots is predominantly lecithin which binds water readily.

Alkali Refining

This process is by far the most important in the refining of drying oils, particularly linseed. Practically the whole line of varnish oils as well as many other grades such as grinding and mixing oils are processed in this manner. This is also true of soybean, fish, and the other drying oils used in the protective coating industry.

Schwarcman (5) describes methods of alkali refining oils, particularly linseed, with emphasis on thorough washing to remove soaps. Gensecke (6) indicates certain advantages obtained by removal of water under vacuum after neutralization of fatty acids. Colbeth (7) discloses design of apparatus for continuous refining of higher viscosity oils such as castor. Thurman and Clayton (8) describe process and apparatus for continuous refining of vegetable oils using caustic soda alone and in conjunction with soda ash. Numerous other patents have been issued on certain features of refining such as bleaching, winterizing, etc.

The purposes of alkali refining are a) removal of non-glyceride constituents, b) production of a neutral oil, c) removal of color bodies, and d) production of oils suitable for further processing into polymerized oils, varnishes, blown oils, and special products. From a theoretical viewpoint it is essential that a process of alkali refining be developed that will produce oils according to the points enumerated above. On the practical side, we are concerned with the most economical procedure that will do the job. Hence the problem must be approached from both sides in order to produce quality oils at lowest cost.

The procedure of refining linseed oil may be divided into the following steps: a) neutralizing, b) removal of soapstock, c) washing of oil, d) bleaching, and e) winterizing.

Neutralization

The neutralizing stage is perhaps the most important part of the refining. This is concerned with the proper choice of alkaline reagent, strength of treating solution, method of addition and proper formation of soap for later removal. From this it is quite evident that preliminary experimental work based on the same type of crude oil is of great value.

In continuous refining of linseed and soybean oils this experimentation is usually done by preliminary runs, adjusting amount and strength of alkaline reagent to produce a soap which will be readily discharged by the centrifuges with minimum occlusion of neutral oil. Once this is effected, the system is practically automatic until a change of crude occurs. However in the batch method of refining it is a constant concern of the refiner to control the process in the right direction.

In the determination of the proper neutralizing procedure for the batch method, choice of alkali is made depending upon grade of oil needed. It is well known that caustic soda will produce oils of light color, low acidity, and good working properties in the varnish kettle. Also it produces soaps which show good solubility in water for purposes of removal with minimum emulsification of neutral oil. On the other hand, soda ash is not as efficient in reducing acidity and does not affect the color nearly as well. Sodium silicate is of use where a compact soap is desired to settle down hard and allow removal of upper oil by pumping.

In linseed refining where the wet method is used, by which soap is removed by washing the neutralized oil, caustic soda is the preferred reagent. The next step is then concerned with the amount of refining agent to use. This is determined by the free fatty acid content of the oil and the amount of foots or gums which are to be removed. Also the action of excess caustic on the color of the refined oil must be taken into consideration. Usually a definite excess of caustic soda solution is used to accomplish the desired results.

The calculation of the amount of caustic soda to use is determined by the following considerations:

a) Acid number of oil equals milligrams of KOH necessary to neutralize free fatty acids in 1 g. of oil. This is equivalent to pounds of KOH per 1,000 pounds of oil.

b) Equivalent quantity of caustic soda is 40/56 of the quantity of caustic potash.

c) Excess caustic soda necessary to precipitate gums and activate color for removal on bleaching.

Example: Crude linseed oil of acid number 2.60 requires per 1,000 pounds of oil:

$$40/56 \times 2.6 = 1.64 \text{ pounds of } 100\% \text{ NaOH}$$

$$\frac{1.64}{.95} \times 1.10 = 1.9 \text{ pounds of } 95\% \text{ NoOH}$$

for 10% excess caustic soda. The excess of caustic may be varied within reasonable limits to meet the situation. However it must be remembered that this tends to saponify the oil with a loss in yield. Hence the excess must be kept to the minimum necessary to accomplish the job.

Next we are concerned with the strength of the refining solution. This is usually determined in conjunction with the neutralization procedure since these factors are closely related. To determine the proper strength of refining solution, several trial runs are made, using the amount of caustic as previously determined. This is made into solutions ranging from 5-20% NaOH since this range is suitable for prac-

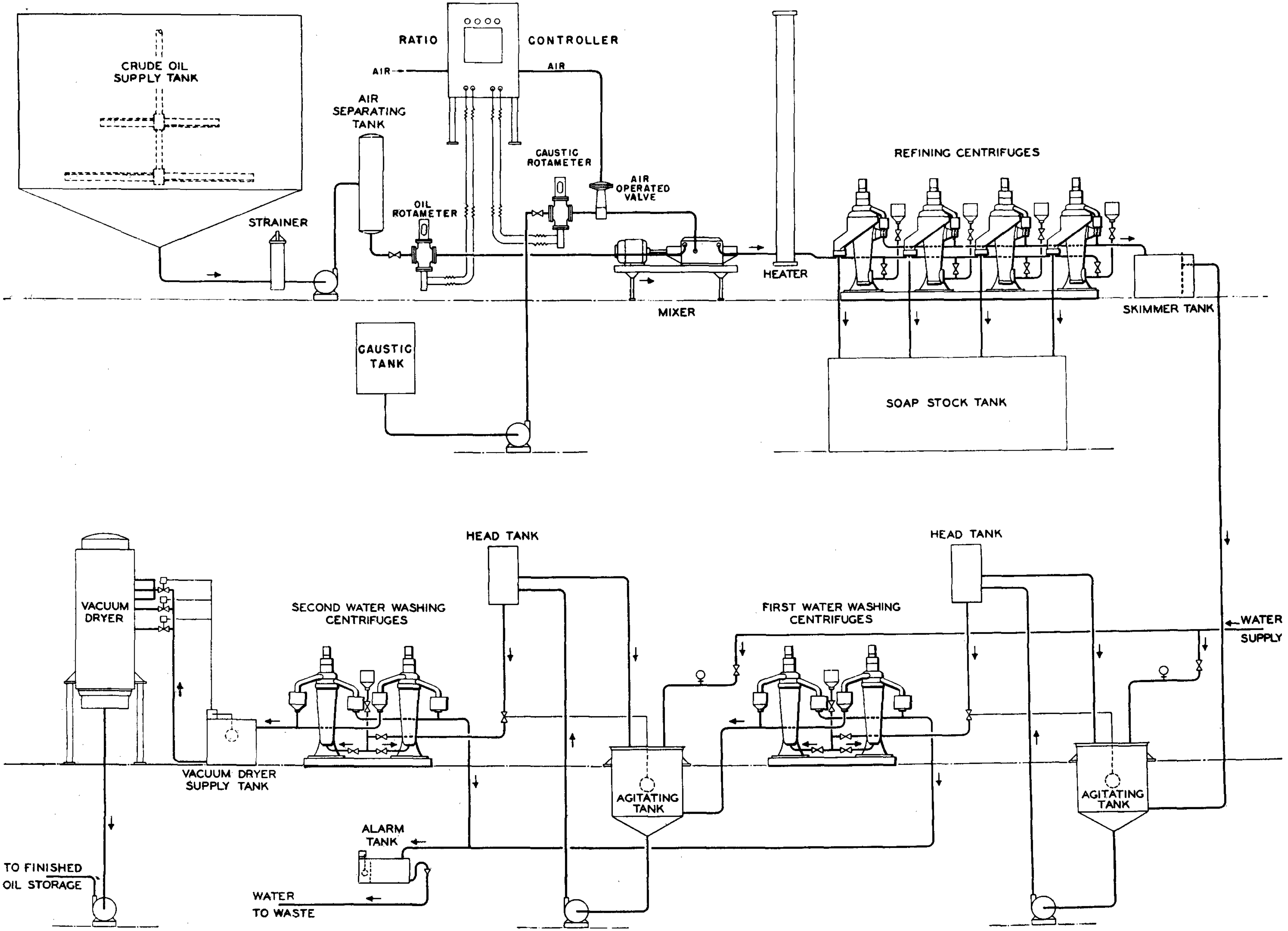

FIG. 2. Flow Sheet—Vegetable oil caustic soda refining, washing, and drying.

tically all crude vegetable oils of normal characteristics. Variation in strength often is necessary since the process of refining includes the degumming of the oil at the same time. Hence, in addition to the water needed for solution of the caustic used for neutralization, it is necessary to have sufficient water present for hydration also. The soap formed in the neutralization step also has a pronounced tendency to precipitate gums and remove them from the oil.

During the trial cuttings a very close study is made of the soap which is produced by neutralization of the free fatty acids of the oil. The proper soap formation determines to a large extent the success of the refining. When first formed at room temperature, it is normally fine-grained, but under moderate agitation and mild heating an agglomeration should occur to large soap flocs which are quick-setting. The soap should break away clean from the oil and precipitate upon stopping the agitation.

At this stage the soap should be in a soft fluid condition which will dissolve quickly and easily in hot wash water. This then forms a thin, dark-colored soap solution which liberates a great deal of neutral oil to the upper oil layer. If the soap appears to be too stiff to flow together on settling, a more dilute or weaker refining solution must be used to obtain a soft, plastic curd.

When the proper strength of refining solution has been determined, the optimum procedure must be worked out. Trial runs are made using the pre-determined quantity and strength of refining solution. This is added to the oil by equal distribution methods with efficient agitation. Agitation is continued while heat is applied until the proper formation of soap occurs. This usually is in the range of 140-180°F. and determines the top temperature of the refining procedure. When the three factors of amount of caustic, strength, and procedure have been determined, we are ready for the next important step in the refining.

Removal of Soapstock

In linseed refining the soap is allowed to settle 30 minutes to 2 hours after reaching top temperature of refining and cutting the agitation. This period is entirely dependent upon the rate of settling of the soap floc. Sufficient time must be allowed to permit it to reach the bottom of the refining kettle. When this has occurred, a hot spray is applied to the surface of the oil without agitation, using an amount of water equal to approximately 5% of the volume of the oil. This is allowed to settle through the oil and contact the bottom soap layer. While maintaining proper temperature on the batch, a period of one to two hours is allowed for solution of the soap in the water. Occasional intermittent agitation is used to promote the action. This is followed with a second similar water treatment, and the batch is allowed to stand for 12-24 hours under heat to complete the solution of the soap.

This step is very critical in determining the yield obtained in the refining. Sufficient time must be allowed to permit maximum solution of soap to form a homogeneous condition. In this state a minimum of emulsion of soap and neutral oil occurs since the solution of the soap will release non-emulsified oil to the upper oil layer.

After the proper settling time has elapsed, the soap solution is drained off the bottom of the tank to be treated further. At this point it is essential that a complete separation of soap from oil is effected. In many crude oils the presence of large amounts of foots or gums will cause the formation of definite emulsion layers between the soap solution and neutral oil layers. These must be efficiently removed from the kettle before the next step in the refining. The usual procedure is to pass the bottom soap solution to a splitting kettle and the emulsion layers to a separate tank for further treatment.

Washing

The refined oil is now ready for the next step; namely, washing to remove all traces of soap and refining solution. This may be accomplished by a variety of means, and care should be taken that no emulsions are formed. Generally several non-agitated hot water sprays are first applied and allowed to settle sufficiently to reach the bottom of the kettle. When well settled, these are drawn off and added to the soapstock for recovery.

The oil is now washed thoroughly with a number of well agitated washes allowing sufficient time to settle before draining and discarding. Washing is continued until it has been determined that all soap and alkali is removed. This may be controlled by either qualitative or quantitative methods which are simple in technique.

Before proceeding to the next step, the bleaching, the oil must be dried so as not to reduce efficiency of the bleaching medium. This may easily be accomplished by vacuum at reduced temperatures or under atmospheric conditions by agitation and heat. The latter method requires substantial surface area of oil to allow for rapid release of moisture. Simple tests may be applied to determine completion of the drying.

Bleaching

This step in the refining is controlled by the specifications of the oils to be produced. The job is accomplished by the use of bleaching earths which adsorb the color through efficient contact with the oil at proper temperatures. This normally takes place in the range of 150-220°F. Batch or continuous methods may be used; the former predominates at present. King (9) describes method and equipment for the continuous bleaching of edible oils such as cottonseed.

In the batch method the dry oil is brought to proper temperature with agitation and the bleaching clay added. These clays may be natural fuller's earth or acid-activated earth; the latter is more efficient in color removal. After sufficient contact under agitation the oil is run to filter presses for removal of the bleaching medium. The filtered oil is pale-colored and practically neutral.

Winterizing

The production of highest grade linseed varnish oils requires the removal of waxes or stearine-like materials present in small amounts in the oil. These materials have decreased solubility in the refined oil, probably because of the removal of protective colloids, and readily precipitate upon cooling. Their removal is desired since their solubility in polymerized oil and varnish is reduced to the point of throwout, causing cloudiness and impairment of gloss in finished products.

Removal is effected by refrigeration of the oil and filtration. Any suitable means of cooling to 30-40°F.

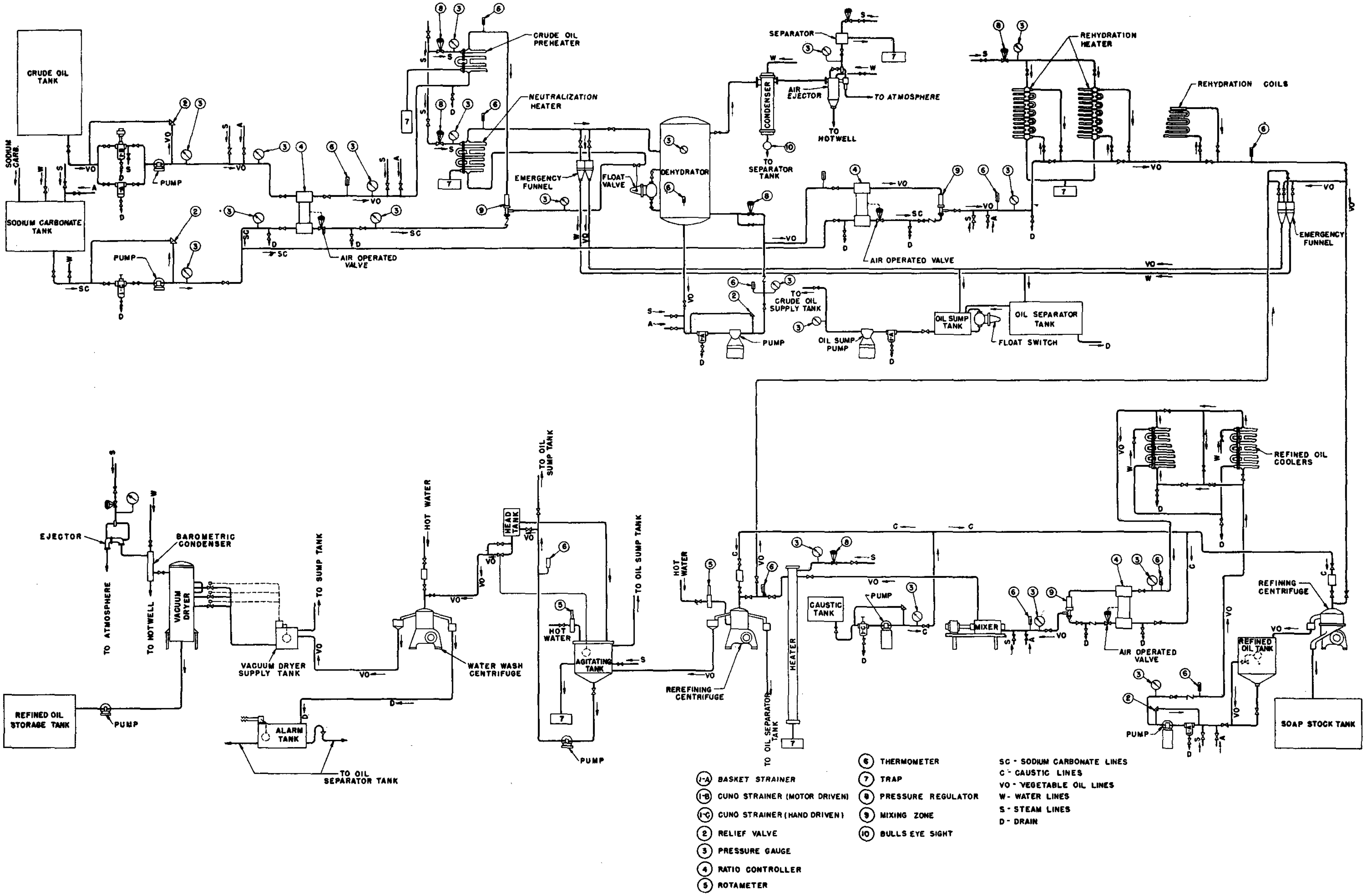

FIG. 3. Flow Sheet—Vegetable oil refining sodium carbonate process with single water wash and vacuum drying.

is acceptable for the purpose. After filtration, the oil will remain clear at temperatures down to 10-20°F. and produces bodied oils having no polymer cloud. Continuous winterizing equipment and layout is also available although batch methods are in general use.

The above covers the batch refining of linseed oil in its entirety. This was described in detail in order to develop and illustrate the nature of the problem and the characteristics of the oil components and products. The continuous method of refining does not allow for close study of the problem as emphasis is placed on equipment. This does not mean that quality is sacrificed since it is generally recognized that this method produces oils equal or better in quality. In addition to continuous operation permitting high capacity per unit of space, the economics of refining are definitely in favor of this method. This is effectively demonstrated by careful determination of refined oil yield and examination of soap stock obtained.

To determine total yield from a batch operation it is necessary to recover all oil possible from emulsion layers, adding the resultant soap solution to the main soap layer. The neutral oil recovered in this operation of emulsion breaking is added to the next batch of crude oil to be processed. The total soap layer is then treated with acid solutions to precipitate crude fatty acids which are termed "Acidulated Linseed Soapstock or Recovered Linseed Oil." This is a very dark-colored oil containing the impurities removed in the refining operation. It is thoroughly washed and dried. In the continuous method there is no emulsion layer hence the total soapstock is removed by the machines and treated as above.

Theoretically, assuming no neutral oil in the final soapstock, the acid number of the recovered oil should approximate that of linseed fatty acids or a value of about 200. This value will be decreased in direct proportion to the amount of neutral oil in the soapstock, which represents loss of yield of refined oil. In other words, an acid value on recovered oil of 100 indicates presence of approximately 50% neutral oil. This, of course, stays with the recovered oil and takes the depreciated value of this material.

From this it is readily seen that the above determination is a convenient tool to use in evaluating the efficiency of the refining. Efforts directed towards increasing the acid value of the recovered oil will result in higher yields of refined oil. The total of refined oil plus recovered oil constitutes total refining yield; the loss of oil through adsorption on bleaching clay and filter aid, etc., accounts for disappearance of oil.

Returning to consideration of efficiencies of batch versus continuous refining of linseed oil, we find that acid values of recovered oils show significant differences. In the former the usual range is 60-110 while, in the latter, values of 100-160 are often obtained. This means that the recovered oil in the batch system contains 45-70% neutral oil while in the continuous this is reduced to 20-50%.

Other Oils

Soybean oil is refined in a similar manner, both in procedure and equipment. On account of the presence of lecithin in quantities up to 2.5%, the oil is often degummed in a separate operation prior to refining. This separation yields a crude lecithin emulsion which is vacuum-dried, bleached, and compounded into commercial products. The oil, which may be nonbreak after this process, is merchandised as such or alkali-refined.

The refining of a previously degummed oil presents some difficulty in separation of soapstock. Due to the removal of gum and the accompanying decrease in free fatty acids by occlusion, the amount of soapstock formed is often too small for efficient separation. This causes trouble both in batch or continuous methods unless steps are taken to increase the quantity of precipitated material. This may be done by addition of other crude oil, fatty acids, or water-binding substances which will mix with the soapstock and become insoluble in the oil.

Continuous degumming and refining of soybean oil are practiced to a large extent in this country today. Plants are in operation with capacities ranging from 1 to 24 tankcars per day. Illustration of equipment and flow-sheet of operations is included in the appendix to this paper. The bleaching and winterizing of soybean oil for technical uses are similar to those for linseed oil.

Fish oil for paints, varnishes, etc., is refined in varying degrees as the requirements demand. The alkali refining of this oil is relatively simple as we are concerned only with the removal of free fatty acids and color. There is no gum or footy matter present to cause complications in separation of soapstock or washing the oil. An accepted procedure is to give the treated oil a hot water spray immediately after formation of the soap. Thus the soap and water settle simultaneously, and rapid soap solution is effected. Sharp separation of soapstock and oil is generally encountered while the washing is a routine matter. Proper destearinization is an important phase of fish oil refining in order to improve drying properties and quality of finished materials.

A relatively new and important contribution to fish oil refining is the application of solvent refining through segregation of the various components. This oil is composed of triglycerides of varying chain length acids, which allows fractional separation under proper conditions of temperature and pressure. Furfural and liquid propane are the solvents currently being used on a commercial scale. During this fractionation, removal of the free fatty acids and color-bodies is effected by concentration into separate fractions. Hence it is possible to produce products having characteristics of alkali-refined oils as well as those of high and low unsaturation dependent upon chain length.

Tung and oiticica oil are not alkali-refined by the industry because of technical reasons. Due to their increased viscosity, emulsification tendencies, and susceptibility to isomeric changes their processing is not feasible. Certain heat treatments suffice to produce suitable changes in these oils attractive to the paint and varnish maker.

Other oils of the drying types used in minor amounts at the present time usually offer no particular problem and are readily processed by established methods.

Acid Refining

The treatment of drying oils, particularly linseed, with inorganic acids for purposes of refining is gradually being replaced by other means. The reasons for this are many, among which the most important are

a) corrosion effects on equipment, b) by-products waste, and c) high acidity of refined oil.

The acid refining is concerned mainly with the use of sulfuric acid in concentrations of 50-85%. The equipment should be lead-lined tanks for batch operation, with steel or wood to support the lining. Agitation may be mechanical or through the use of air sparge.

The oil is treated with quantities of acid ranging from .1 to 2% depending upon its crude condition. Temperatures of 80-120°F. are used; cooling is applied whenever exothermic conditions become evident. The diluted acid does not sulfate the oil but has a severe charring action on the other organic material present. This action manifests itself in the formation of black particles which coalesce and precipitate to form a tarry residue. After sufficient settling time, the oil is siphoned off and sometimes given a lime treatment to neutralize residual acid. More frequently it is thoroughly washed and dried in the usual manner. Bleaching is also accomplished as previously described. The acid residue is discarded as no commercial use for it has been developed as yet.

Refining Equipment

Batch Method. The equipment for this method may be either open or closed-top tanks fitted with conical bottoms. Two-speed agitation of 20-40 r.p.m. is used with enough mixing blades on a vertical shaft to insure thorough contact of oil and treating agents as well as wash water. Spray rings are located at the top of the tank for addition of refining agents and water. Coils or jackets may be used for steam or water heating and cooling.

Continuous Method. The oil and refining solution are metered continuously for proper proportioning. The two liquids are then introduced to a mixing chamber, where vigorous agitation insures complete and thorough contact for soap formation. The mixture then passes to a heating chamber to prepare the soap for proper processing. The combination next flows to the soapstock centrifuges where continuous separation of oil and soap occurs. The soapstock is discharged to a catch tank while the oil flows to the water mixing chamber. Here it is washed by rapid mixing with hot water and properly metered, prior to passing to the water-wash centrifuges where separation of oil and water takes place. Single or double water-washing stages may be employed depending upon the requirements of the refiner. The oil next flows to the vacuum flash drier, where the residual moisture (approx. .15%) is removed continuously and the oil is pumped to bleaching tanks.

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Fractionation of Drying Oils and Acids

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DURING the past 10 to 15 years good chemical engineering has been combined with drying oil technology to produce a number of methods of increasing the degree of unsaturation of a fatty oil or fatty acid. An attempt will be made to briefly review those methods of fractionation which are currently in commercial operation. It is obvious that only the general principles of operation can be covered in this one 40-minute session.

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These processes may be divided into the following classifications:

- a) liquid-liquid fractionation
  - 1. furfural process
  - 2. liquid propane process
- b) fractional crystallization
- c) fractional distillation

The products produced by these processes have aided the drying oil chemist in his choice of raw materials.

Liquid-Liquid Fractionation

Furfural Process. Liquid-liquid fractionation of a glyceride oil with furfural is dependent upon the fact that oils are only partially miscible with furfural at normal temperatures. If the temperature were to be raised, complete miscibility of the oil and furfural would eventually result and the process would become inoperable. When a glyceride oil and furfural are contacted however, at a temperature below that of complete miscibility, two phases are obtained, a solvent predominant phase and an oil predominant one. It has been found (1, 2) that the more unsaturated glycerides concentrate in the solvent predominant phase, or so-called extract phase, with the more saturated glycerides in the oil predominant or raffinate phase. The degree of separation effected by a single stage batch separation is rarely sufficient in producing fractionations of commercial significance. Separations of this type require multiple batch separations or continuous countercurrent extraction with the use of reflux.

In order to obtain efficient fractionation it has been found that continuous countercurrent methods are the most economic. A simple countercurrent system is illustrated in Figure 1 (3).