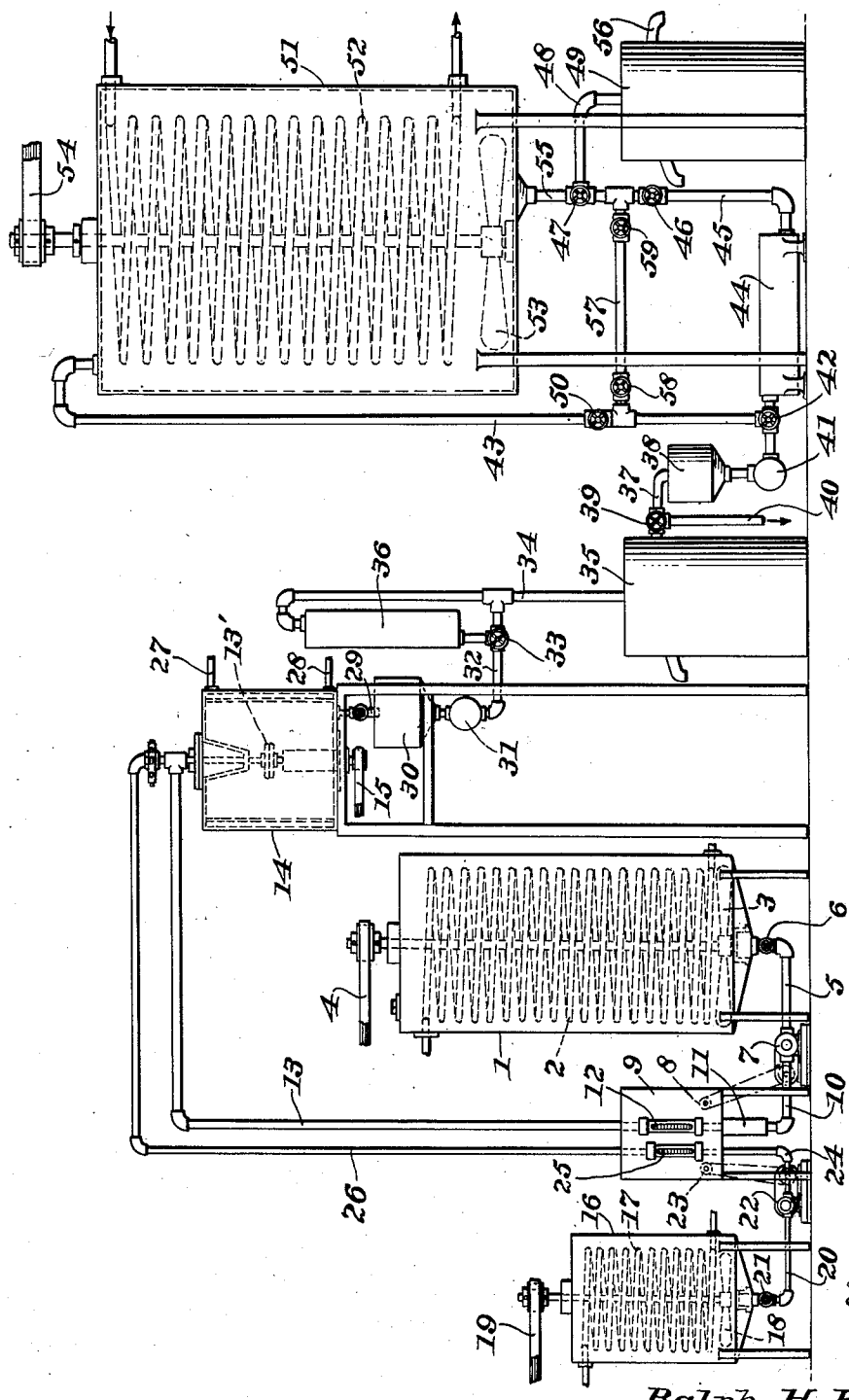
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REFINING METHOD AND APPARATUS

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REFINING METHOD AND APPARATUS

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2 Claims. (Cl. 260—425)

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This invention relates to the refining of glyceride oils for the purpose of removing the free fatty acids and colloidal matter such as color particles and other colloidal impurities. A principal object of the invention is to reduce the refining loss and to produce a refined oil, or a re-refined oil, which is low in color and contains less impurities than is possible using prior methods. Another object of the invention is to produce a clarified refined oil. Another object of the invention is to facilitate the centrifugal separation of the oil-soapstock mixture, produced in accordance with the invention, by enabling such an excess of caustic alkali to be used that a two-layer soapstock forms in the centrifuge. Since the process involved applies in the same manner to all animal and vegetable oils, I shall hereinafter discuss it, by way of example, in connection with the refining of cottonseed oil, and it will be understood that the described procedure is typical.

This application is a continuation-in-part of my application Serial No. 522,135, filed February 12, 1944, now abandoned.

In my Patent No. 2,342,042 of February 15, 1944, I have set forth my discovery that the colloidal impurities in cottonseed oil are positively electrically charged and, based on this discovery, I have disclosed a new refining procedure fundamentally involving the mist-mixing of the oil and refining agent. In the practice of this mist-mixing process, the superior results, as regards color removal and reduction in refining loss, are attributable to the fact that the refining agent reacts with the free fatty acids in the oil to form a colloidal soapstock whose particles are negatively charged and, as a result of the interspersion of these soapstock particles with the positively charged colloidal particles in the oil, the latter are rendered electrically neutral and will thus precipitate so as to be separable in large part with the soapstock. In this latter connection, I have taught, in my said patent, that the alkaline refining agent must be used in an amount in excess of that theoretically required to neutralize the free fatty acids in the oil, this for the purpose of maintaining a high pH up to the time of separation so that the solution of electrically neutralized colloidal particles in the neutral oil is reduced. In speaking of the maintenance of a high pH, I mean a pH of the order of that of caustic alkali, namely 13. The maintenance of the pH, by reducing or preventing the solution of electrically neutral colloidal particles in the oil, also reduces the formation of a water-in-oil emulsion which would give a dirty oil and would

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increase the refining loss by occluding neutral oil with the soapstock.

The soapstock obtained by my mist-mixing procedure, as described in my said patent, ordinarily contains from 20% to 30% neutral oil. In the continuous processes of refining now in use, utilizing liquid mixing, the soapstock shows from 1% to 10% neutral oil when analyzed, but these figures do not represent the actual neutral oil content of the soapstock as formed. Actually the low neutral oil content shown by analysis is due to a large excess of caustic soda not being entirely consumed before the soapstock is separated from the refined oil, and as a result, this excess caustic soda saponifies some of the neutral oil in the soapstock, thereby lowering the neutral oil content in the soapstock. In the process according to my said application, the caustic soda is ordinarily used in such slight excess that very little is carried over into the soapstock and, consequently, the neutral oil content of the soapstock is substantially the same upon analysis of the soapstock as when the soapstock was formed.

Various processes have been proposed for reducing the refining loss occasioned by the holding of neutral oil in the separated soapstock. Chisholm in his United States Patent No. 1,007,642, uses sodium silicate to reduce the refining loss. (Unless otherwise specified, the term sodium silicate as used herein means commercial sodium silicate, commonly known as water-glass. When the term sodium silicate is used between quotation marks, it refers to the compound contained in sodium silicate, which latter also contains colloidal silica.) In his United States Patent No. 1,010,017, Chisholm uses sodium aluminate, sodium zincate, or sodium ferrite. In using sodium silicate, Chisholm added added 40° Bé. sodium silicate mixed with a 16° Bé. caustic soda in various proportions to the oil being refined in an amount substantially to neutralize the free fatty acids, and be subsequently added the amount of caustic soda solution normally used in the ordinary process of kettle refining. The refining loss obtained in some cases was lower than could be obtained in the ordinary kettle process. In other cases there was no reduction in the refining loss compared with the results obtained by the ordinary kettle process. The color of the refined oil produced was, in practically all cases, darker than that obtained in the ordinary kettle process. The refined oil resulting from the Chisholm process using sodium silicate was muddy in appearance because of a large amount of small particles of soapstock in suspension. This in-

ability to control results in the use of the Chisholm silicate process limited the use of the process to such an extent that its practice was finally abandoned. The mechanism of the Chisholm process which resulted in reducing the refining loss in the case of some oils was not understood and therefore no modification of the procedure was developed which would permit of the successful application of the Chisholm process to all glyceride oils. Chisholm's process using sodium aluminate, etc., was never practiced commercially. These later reagents were proposed merely as being non-oil-saponifying and with no aim of reducing the retention of neutral oil in the soapstock.

The use of sodium silicate in the continuous processes of refining now practiced has been tried, but without success, and, in my opinion, one reason for this is because all of the caustic soda solution required in the refining process has been added simultaneously with the sodium silicate. This is in contrast to the Chisholm process according to which, as above stated, the major portion of the caustic soda solution was added after the addition of the sodium silicate. In the two U. S. patents to Holbrook, Nos. 1,169,154 and 1,169,155, one process requires the addition of the sodium silicate with all of the caustic soda solution, and in the other the sodium silicate is added after the caustic soda solution has been added in amount substantially sufficient to neutralize the free fatty acids in the oil. Neither of the Holbrook processes would reduce the refining loss as would the Chisholm process. This lack of success when using sodium silicate according to the two Holbrook processes and when using sodium silicate in the continuous process of refining now in use, when compared with the success of the Chisholm process on some oils, affords the basis for a definite theory of the mechanism of the Chisholm process, as follows:

Commercial liquid sodium silicate contains hydrous colloidal silica. When the sodium silicate, mixed with a small amount of caustic soda solution, is added to the crude oil being refined, in accordance with Chisholm's procedure, some of the sodium silicate reacts with the free fatty acids in the oil forming an additional small amount of colloidal silica. The colloidal silica thus present adsorbs some of the caustic soda solution subsequently added. The dark color of the refined oil obtained is due to the retardation of saponification of neutral oil by reason of the adsorption of the caustic soda solution by the colloidal silica, and as explained in my above-mentioned patent, in refining processes involving liquid mixing, color removal occurs as a result of the saponification of neutral oil whereby is formed a negatively charged colloidal suspension which acts to electrically neutralize the positively charged colloidal particles in the oil so that they are precipitated. The reduction in refining loss obtained in some cases by the Chisholm process is due to the combined action of the colloidal silica and "sodium silicate" present in the commercial liquid sodium silicate. Both the colloidal silica and "sodium silicate" adsorb water thereby reducing the retention of neutral oil in the soapstock as an oil-in-water emulsion. In addition, the colloidal silica adsorbs caustic soda solution thereby retarding the rate of saponification of the neutral oil, and there is also adsorption of the caustic solution by the "sodium silicate." My theory of retarded saponification being correct, it would follow that in the use of my mist-mixing procedure, which relies on the colloidal soapstock formed by the neutralization of the free fatty acids for major color removal in the refining of crude oil, retarded saponification could be utilized for its beneficial results while still obtaining the necessary color removal.

In order to test the above theory, I refined a crude cottonseed oil, using the continuous mist-mixing procedure of refining as described in my above-mentioned patent, with crystallized sodium meta-silicate dissolved in an amount of caustic soda solution sufficient for refining. This sodium meta-silicate contained no colloidal silica and, since I added it simultaneously with all of the caustic soda solution required to refine the free fatty acids, no appreciable amount of colloidal silica was formed by the action of the free fatty acids in the oil. A second test was made with crystallized sodium meta-silicate and colloidal silica mixed with the amount of caustic soda solution necessary for refining. The colloidal silica was added in the form of silica jelly. A third test was made with only silica jelly added to the caustic soda solution, with the latter again in amount necessary for refining. In all of the tests, practically the same amount of excess caustic was used and all the other conditions of the tests were the same. The following are the results of the three tests:

Test No.	Loss	Color	Neutral Oil in Soapstock Dry Basis
	Per Cent		*Per Cent*
1	4.8	35.0 Y-5.5 R	6.5
2	4.1	35.0 Y-5.1 R	5.3
3	4.9	35.0 Y-5.5 R	6.5

The fact is to be noted that the lowest refining loss, best color, and lowest neutral oil in the soapstock resulted where there was the combined effect of the crystallized sodium meta-silicate and the colloidal silica. A laboratory test on the same crude oil, using caustic soda, only, gave a refining loss of 7.0% and a color of 35.0 yellow-4.9 red. Thus, in each of the three tests utilizing mist-mixing the refining loss was less than in the laboratory test.

In the tests utilizing mist-mixing, the amount of colloidal silica used was about 0.03% based on the weight of the oil, the amount of crystallized sodium meta-silicate was 0.25% based on the weight of the oil, and the excess caustic was .4%. The temperature of the oil at the time of mixing was about 110° F. and the temperature at the time of leaving the reaction chamber was about 180° F.

I have added larger amounts of silica jelly to the caustic soda solution used in refining cottonseed oil by my mist-mixing process. The refining loss and the neutral oil content of the soapstock was reduced below that obtainable without the use of silica jelly. The color of the refined oil obtained was darker than that produced without the use of silica jelly as would be expected in view of the increased saponification retarding capacity. The silica jelly contained approximately 9% silica. I added 20%, 30%, 40% and 50% of the jelly, based on the weight of the caustic soda solution, to caustic soda solutions having concentrations of 32.5%, 37.1%, 43.3% and 52% respectively so that the resultant solutions had concentrations of about 26% caustic soda. I found that as the per cent of colloidal silica used increased, the per cent of moisture in the refined oil obtained decreased. For example,

in the above tests, the moisture content of the refined oil dropped from 0.16% when using 20% silica jelly to 0.10% when using 50% silica jelly. The neutral oil content of the soapstock varied from 10.2% in the refining using 20% silica jelly to 6.5% in the refining using 50% silica jelly.

I have successfully used as little as one-half per cent of sodium silicate, based on the oil being refined, added to the caustic soda solution when refining crude cottonseed oil by my continuous mist-mixing process, and I have found that the best results are obtained when the sodium silicate has a high ratio of silica to sodium oxide, for example, 3.9 to 1. The concentration of the caustic soda was about 26%. The refining loss was as low as that obtained using 20% to 50% silica jelly added to the caustic soda. I attribute the fact that I can successfully use sodium silicate in the mist-mixing process of continuous refining while sodium silicate when used in present day processes of continuous refining cannot be successfully used, to the fact that in my process the moisture content of the soapstock is less than that of soapstock produced in the present day process of continuous refining, which means that less colloidal silica and "sodium silicate" are required to reduce the formation of an oil-in-water emulsion in the soapstock. Therefore, the amount of colloidal silica and "sodium silicate" present in the sodium silicate plus the amount of colloidal silica formed in the refining operation using my mist-mixing procedure is sufficient for the purpose of reducing the amount of oil-in-water emulsion formed in the soapstock. If the amount of sodium silicate required to reduce appreciably the formation of the oil-in-water emulsion in the soapstock were used in present day continuous processes, the colloidal silica and silicate anion thus introduced would adsorb such a large amount of caustic soda that the refined oil produced would be extremely dark.

In tests 1 and 3, hereinbefore referred to, the refining loss is practically the same, confirming that the "sodium silicate" has an adsorptive capacity for caustic soda. Because of its water adsorptive capacity it adsorbs the caustic solution and so acts as a saponification retardant. However, per unit weight it is not as effective as colloidal silica in this respect.

The amount of the retardant (water-adsorbent) required will vary with the available surface of the retardant. Where the retardant is in colloidal form, the greater the degree of its dispersion the less of the retardant is required to effectively reduce the rate of saponification of the neutral oil. Colloidal suspensions, such as chromic oxide or silica jelly, have the effective surfaces of their colloidal particles reduced on aging so that as these suspensions become older, more of the suspensions would be required to effectively retard saponification of neutral oil than when the suspensions are freshly made.

In the case of compounds having only water adsorptive anions, the saponification-retarding and water-adsorptive effects are much less than in the case of the colloidal suspensions referred to above and, hence, to produce an equal saponification-retarding action, much larger amounts of these compounds are needed.

In ordinary high ratio silica to sodium oxide water glass, the colloidal silica content is approximately 50% of the total silica content. Where freshly made silica jelly was used in refining a low free acid oil, satisfactory results were obtained when only an amount of silica jelly was used which contained colloidal silica equivalent to .03% of the oil being refined. When using commercial water glass of the character indicated above, .5% of the water glass, based on the oil, was used which was equivalent to using approximately .06% of colloidal silica plus .06% of "sodium silicate." The reason that more of the colloidal silica contained in the water glass was required than was necessary when the fresher silica jelly was used, is due to the greater degree of dispersion of the colloidal silica in the silica jelly than in the water glass. The saponification-retarding action of the water glass was due to the combined action of the .06% colloidal silica and the .06% "sodium silicate."

The proportions of excess caustic and sodium silicate required to be used varies with the refining loss; the greater the refining loss the greater the proportions of excess caustic soda and sodium silicate required. In the mist-mixing process of refining without the use of sodium silicate or other water-adsorptive agent when refining crude glyceride oils usually found in commercial practice, an excess caustic of from 0.2% to 0.3% is ordinarily sufficient. Occasionally, oils are encountered which contain an abnormal amount of colloidal material which assists in increasing the rate of saponification of the neutral oil thereby more rapidly consuming the excess caustic. In order to have a high pH at the time of the separation of the refined oil from the soapstock in this type of oil, an excess of caustic of more than 0.3% is required.

The amount of sodium silicate, having a ratio of silica to sodium oxide of 3.9:1, which usually should be used in refining ordinary crude glyceride oils is approximately one-thirteenth of the refining loss obtained by the official cup test of the American Oil Chemists' Society. With an oil having a refining loss by the official cup test of 6.5%, I have successfully refined the oil by the continuous mist-mixing process of refining disclosed in my aforementioned patent using 0.5% of 3.9:1 sodium silicate and 0.5% excess caustic soda, both based on the oil being refined. Where the refining loss varies from 6.5% by the official cup test, the following formula will usually give a satisfactory approximation of the proportion of excess caustic soda that is to be used:

$$Y(\text{excess}) = 0.3 + \frac{.4a}{13}$$

where a is the per cent of refining loss by the official cup test.

One of the problems in the present day practice of the continuous re-refining of glyceride oils is the prevention of the formation of a two-layer soapstock. The extra layer consists of excess caustic solution which accumulates in the centrifuge, where the refined oil is to be separated from the soapstock, preventing the discharge of the soap. This results in the trapping of a layer of soap between the layer of caustic solution against the bowl wall and the refined oil being discharged. When this layer of soap becomes too great, the soap discharges with the refined oil. This trapping of soap occurs because the proportion of free caustic solution to soap is large. In my said patent I prevent the formation of a two-layer soapstock in re-refining by using only a slight amount of excess caustic and also by interpolating a time period between the reaction chamber and the separating centrifuge, which results in reducing the excess caustic.

In present day practice of the continuous re-

fining of crude glyceride oils a hard layer of soapstock accumulates on the bowl wall. The increase in the thickness of this layer results in decreasing the effective diameter of the bowl thereby reducing the centrifugal force being applied on the soapstock discharged from the centrifuge. This condition results in an increase in the neutral oil content of the soapstock as a run proceeds. To overcome this condition, the present day practice is to clean the soapstock layer from the centrifuge bowl at least once a day. This decreases the capacity of a plant as well as reducing the efficiency of operation by reason of the gradual increase in the neutral oil content of the soapstock being discharged during a run. It is my opinion that this accumulation of soapstock on the bowl wall is due to the roughness of the wall which retards the flow of the soapstock. This retardation results in the soapstock against the bowl wall being subjected to the maximum centrifugal force of the bowl for a longer period of time than the main bulk of the soapstock thereby reducing the neutral oil content of this retarded soapstock which results in increasing its specific gravity. By lining the bowl of the centrifuge with a smooth layer, this accumulation of soapstock can be prevented. The polishing or plating of the bowl wall would accomplish this result but any abrasion of this finish in the normal cleaning operations performed when the centrifuge is shut down would initiate the formation of this undesirable soapstock layer.

I have found that by lining the bowl with a liquid, the liquid affords a perfect surface which facilitates the movement of the soapstock from the bowl and prevents the formation of the undesirable layer of soapstock. Thus at all times, the soapstock being discharged is subjected to practically the maximum centrifugal force of the bowl and it is not necessary to shut down the centrifuge to clean the bowl.

When a considerable excess of caustic solution is used in refining by my mist-mixing process of refining crude glyceride oils, a two-layer soapstock is formed similar to that obtained in the re-refining of glyceride oils, however differing from the two-layer soapstock obtained in the latter case in that the proportion of free caustic solution to soap is small. Because of this condition, the velocity of discharge of the soapstock carries some of the free caustic solution which accumulates on the bowl wall along with the soap thus preventing the continued accumulation of the free caustic solution layer. Thus the bowl wall becomes lined with a liquid layer of free caustic solution over which the soapstock moves without touching the bowl wall, thereby preventing the formation of the undesirable soapstock layer.

If, in the absence of a saponification retardant, sufficient excess caustic is used to produce the layer of free caustic solution, the refining loss is increased by reason of the increased saponification of neutral oil. By using the retardant I am enabled to produce the layer of free caustic solution while controlling the saponification of neutral oil and holding it at a minimum.

The following formula gives an approximation of the excess caustic required to produce a layer of free caustic solution on the bowl wall when sodium silicate is used:

$$Y(\text{excess}) = .6 + \frac{.4a}{13}$$

where a is the refining loss by the official cup test of the American Oil Chemists' Society.

When a caustic soda solution is used in refining glyceride oils, particles of soap are formed. The excess caustic solution is distributed throughout these soap particles. The concentration of the caustic solution on the surface of these soap particles is reduced by saponification of neutral oil. When a saponification retardant is not present, the caustic in the interior of the soap particles diffuses rapidly to the surface of the particles, the rate of diffusion decreasing as the difference in concentration of the caustic between the surface of the particles and the interior decreases. Thus eventually the concentration of the caustic on the surface of the particles arrives at a point where the soap particles will fuse together even though the concentration of the caustic in the interior of the particles is still such as would prevent coalescing if the concentration occurred on the surface of the particles. When a saponification-retardant is present, the rate of diffusion of the caustic from the interior of the soap particles to the surface is retarded so that when coalescence occurs, the concentration of caustic in the interior of the soap particles is greater than is present at the time of coalescence when no saponification retardant is used. This coalescence of the soap particles when no saponification retardant is used commences to some extent as the oil-caustic mixture is leaving the reaction chamber, as indicated by the size of the soap particles. When a retardant is used, the soap particles are smaller at the time the oil-caustic-retardant mixture leaves the reaction chamber. This smaller size of the soap particles is due to the greater concentration of caustic present at the time the mixture leaves the reaction chamber as compared to that present when no retardant is used, and this concentration prevents the fusing of the soap particles. The greater concentration present is due to the saponification retarding action of the water adsorptive material present and to the greater excess caustic used when a retardant is present.

When sufficient excess caustic is used, together with a retardant, which results in the formation of a two-layer soapstock in the refining centrifuge, very little agglomeration of the soap particles occurs before the mixture enters the refining centrifuge because the large excess of caustic maintains too high a concentration of caustic on the surface of the soap particles to permit major agglomeration. The major coalescence of the soap particles under these conditions must occur in the separating centrifuge after the free excess caustic solution is formed into a separate layer under the action of centrifugal force. Since the water adsorptive retardant contained in the body of the soap particles has adsorbed to it a concentrated caustic solution, the water in this solution is not available to form an oil-in-water emulsion with the neutral oil. This concentrated caustic solution cannot form an emulsion anymore than the concentrated solution contained in the separated caustic solution layer in the centrifuge could form an emulsion with the oil before being separated. This lack of ability to emulsify with the neutral oil is due to the insolubility of the soap in concentrated caustic solutions. Concentrated caustic solutions can be used to "salt out" soap from soap solutions in the same manner that common salt "salts out" soap from soap solutions. Therefore, the only water available to form an oil-in-water solution

in the soapstock from the neutral oil is that water on the surface of the soap particles whose caustic concentration has been reduced sufficiently to permit the soap particles to coalesce. Therefore, the soapstock has only a low neutral oil content.

In the continuous processes of refining now in use, the oil-caustic mixture is usually heated to about 140° F. to obtain a break before separating the refined oil from the soapstock. If the mixture were heated to from 180° F. to 200° F. more caustic soda would be required so that excess caustic would be present at the time the oil is separated from the soapstock. This excess caustic would result in increasing the refining loss. However, when using sodium silicate mixed with the caustic soda solution, by reason of the adsorptive effect of the colloidal silica and silicate anion for caustic soda, the rate of saponification of the neutral oil is retarded, in accordance with the present invention, so that the oil-caustic soda mixture can be heated to temperatures such as 180° F. to 200° F. prior to the separation of the oil and soapstock, without materially increased saponification of neutral oil by the excess caustic.

In the mist-mixing process of refining, according to my said patent, an excess of from .2% (usual) to .3% caustic is used and the mixture is heated in the reaction chamber to a temperature of about 140° F. If the mixture were heated in the reaction chamber to 160° F. using the above amount of excess caustic, the increased rate of saponification occasioned by the use of the higher temperature would reduce the pH of the mixture so that by the time the mixture arrived at the refining centrifuge, an incomplete separation would result. Logically, one could then reason that by using a lower temperature in the reaction chamber, say 120° F., less than .2% excess caustic could be used satisfactorily. This is not true because at the lower temperature the soapstock formed would not be sufficiently fluid to fuse together thereby causing pockets of oil to be occluded in the soapstock. If a temperature of 160° F. or higher were used it would be necessary to use more than .3% excess caustic in order to have a proper pH present in the refining centrifuge. By adding a saponification retardant such as sodium silicate, high temperatures can be used because the saponification retardant, by reducing the rate of saponification, prevents an increase in the refining loss. At these high temperatures in the presence of a saponification retardant, a large excess of caustic can be used which excess is adsorbed by the saponification retardant, thus permitting the reduction of the concentration of the caustic on the surface of the soapstock which will allow the soapstock to fuse together readily at the high temperatures used without the saponification of a large excess of oil because the excess caustic is adsorbed by the saponification retardant.

As previously stated, on some oils the Chisholm process did not reduce the refining loss. These oils were oils that had a low refining loss already, which low refining loss was due to a low neutral oil content in the soapstock. Chisholm used the maximum amount of sodium silicate that would not materially affect adversely the color of his refined oil. This means that the amount of sodium silicate was insufficient to reduce materially the neutral oil content of the soapstock. If he had used more sodium silicate (water glass), there would have been present a greater quantity of colloidal silica and silicate anion which would have given him a bad color by reason of the saponification retarding action of these compounds. In my process, I am able to operate at much higher temperatures before separating the oil from the soapstock and thereby am able to use more sodium silicate and still obtain a satisfactory color, because the higher temperatures permit of a more efficient removal of coloring matter. I therefore am able to refine oil by my process satisfactorily.

In the continuous processes of refining now in use and in the old kettle process, the oil at the beginning usually has a temperature of from 70° F. to 90° F. The temperature at which the break occurs, namely, where the oil and soapstock separate readily, varies with the type of oil and the equipment used. In the case of kettle refining, this temperature is usually from 120° F. to 130° F. When sodium silicate is added to the caustic solution, the breaking temperature is from 110° F. to 120° F. In the continuous liquid mixing process of refining, the breaking temperature is usually from 135° F. to 140° F. The mechanism of the break has not been heretofore understood in the refining industry. No explanation has been offered as to why the rate of heating, for example, varies the breaking temperature. As a result of my experience with mist-mixing refining, I have ascertained the mechanism which results in producing the break, the details of which are given above.

When the caustic soda solution used in refining is added to the oil being refined, the resulting mixture is ordinarily called an emulsion. In my opinion, it is not an emulsion but consists of fine soapstock particles suspended in the oil. According to my theory, on heating and agitating this suspension, the particles of soapstock agglomerate, producing the so-called break. This agglomeration can occur independently of temperature. With the same oil and the same amount and strength of caustic solution, the temperature at which the break occurs can be controlled by the rate of heating and the rapidity of agitation. The break is determined by the concentration of the caustic soda solution on the surface of the soapstock particles. When this concentration is reduced sufficiently, the soapstock particles will fuse together causing the break. With slow heating of the oil-caustic soda mixture, the concentration of the caustic soda on the surface of the soapstock particles is reduced to the agglomeration concentration at a lower temperature than when the heating is rapid. Thus the same oil-caustic mixture can be broken at 110° F. or 140° F. depending upon the rate of heating, keeping the agitation constant.

The rate of saponification of neutral oil by the excess caustic soda increases with an increase in temperature. If the mixture is heated too high before separating the soapstock from the oil, all of the excess caustic soda will be consumed thereby reducing the pH of the mixture. Because of this reduction of pH, more of the electrically neutral colloidal material will be dissolved in the oil, resulting in the formation of a water-in-oil emulsion with the soapstock as the water phase. This causes the soapstock to contain more neutral oil. In order to increase the temperature at which the oil and soapstock can be separated satisfactorily from each other, more excess caustic is required. The use of more excess caustic in the kettle refining process and in the continuous process utilizing liquid-mixing results in increas-

ing the refining loss because of the saponification of neutral oil by the excess caustic. The use of a higher temperature of the oil-caustic soda mixture than is now the practice at the time of separation of the oil and soapstock is desirable because it facilitates the separation and a lower colored, cleaner oil is obtained.

I have found that by the addition to the solution of caustic soda of a saponification-retardant which is effective by reason of its adsorptive capacity for the caustic soda solution, a higher temperature can be used at the time of separation without an increase in refining loss. As above stated, I have found colloidal silica to be a suitable saponification-retarding agent by reason of its adsorptive capacity for the caustic soda solution. Instead of adding the colloidal silica as such, it may be produced from silicon compounds by the reaction of such compounds, soluble in glyceride oils, with caustic soda. Examples of such compounds are: Methyl silicate, trimethylethoxy-silicon, hexamethoxy-disilicon, and (trimethoxy silicon) (triphenoxy silicon) oxide. Other examples of suitable substances for this purpose are chromic oxide, zirconium oxide, lead peroxide, titanium dioxide, i. e., hydrous oxides which are dispersible directly or indirectly in caustic alkali. Hydroxides are also usable for the same purpose and among these may be mentioned nickelous and cadmium hydroxides.

Zirconium oxide, above mentioned, cannot be dispersed as a colloidal suspension by means of caustic alkali as can, for example, chromic oxide, but it may be dispersed in a caustic alkali solution by the use of a colloid mill. This same procedure can be used in the use of nickelous and cadmium hydroxides.

It may be mentioned that various procedures are known for obtaining colloidal suspensions of oxides and hydroxides of metals which ordinarily would be precipitated when caustic alkali is added to solutions of salts containing such metals. For example, potassium tartrate used in conjunction with potassium hydroxide will form a sol of nickelous hydroxide; cadmium hydroxide can be obtained in colloidal solution by using hot concentrated potassium hydroxide.

Hydrous oxides and hydroxides are, of course, water adsorptive. As has been stated hereinbefore, the silicate anion of "sodium silicate" has a water adsorptive capacity and a saponification retarding action. Other salts whose anions produce similar results are the alkali aluminates, stannates, vanadates, tungstates, titanates, and zincates; in general salts having an anion which is water adsorptive. More particularly, I use a compound having an anion containing an element of a character which is capable of forming a hydrous oxide, this capability being mentioned by way of definition only since it may not necessarily be exercised in the refining process. However, it is my opinion that in the use of sodium aluminate, for example, a small amount of oxide is temporarily formed and that this fugitive oxide aids in the color reduction. The bleaching effect of clays, both acid treated and untreated, on refined vegetable oils has been attributed to adsorption of the color substance by hydrous aluminum silicate present in the clays. Hydrous oxides, metallic and non-metallic, are used as mordants in dyeing where they adsorb coloring matter to form lakes. Silicon is a non-metal. The use of a hydrous metallic colloidal oxide, either added as such or formed as above mentioned in connection with sodium aluminate, results in a better adsorption of the coloring matter so that the refined oil obtained will be lighter in color than that obtained using hydrous colloidal silica.

The effect obtained by reason of the water adsorptive power of the reagents, i. e., a reduction in the neutral oil content of the soapstock is a very valuable one. The neutral oil present in soapstock occurs as an oil-in-water emulsion and also as a water-in-oil emulsion, the soapstock constituting the water phase in the latter case. By reason of the water adsorptive power of the reagents, the formation of an oil-in-water emulsion is reduced to such a point that as little as 2% neutral oil remains in the soapstock as compared with the normal amount of from 20% to 30%.

The saponification retarding and water adsorptive agent may be introduced with the caustic solution or may be otherwise introduced as will be hereinafter mentioned.

In operating under the present invention using a saponification-retarding agent with my mist-mixing process, an excess of caustic is used beyond that normally used in the practice of the invention as described in my aforementioned patent. By heating to 180° F.–200° F. and keeping the oil and refining-solution mixture agitated, some of the excess caustic adsorbed by the colloidal silica and silicate anion slowly saponifies neutral oil thereby resulting in reducing the color of the oil by removing some of the highly dispersed color suspensoids, this action, of course, being auxiliary to that of the colloidal soapstock formed from the free fatty acids. This procedure differs from all other refining procedures. In the latter, the removal of the highly dispersed color suspensoids occurs at relatively low temperatures and depends upon the slow saponification of neutral oil by reason of the low temperatures to effect the contacting of the negative electrical charges on the soap formed with the positive electrical charges on the color suspensoids present in the oil.

In my process, the adsorption of the caustic solution by the retarding agent permits the use of a high temperature to effect the saponification of neutral oil which results in the removal of additional highly dispersed color suspensoids.

The temperature effect is a factor not only of the breaking temperature but also of the temperature at which the oil and refining agent are mixed. Ordinarily the temperature of the oil at the time it is mixed with the refining agent is from 70° F. to 90° F. If higher temperatures were used under present day refining practices, the refining loss would be increased and darker colored oils would be obtained by reason of the rapid saponification of neutral oil and the rapid agglomeration of the soapstock thus formed. When a saponification-retarding agent is presented in the caustic solution, higher temperatures than the above may be used by reason of the presence of this agent. I have successfully mixed the oil and caustic solution when the oil was at a temperature of 160° F., subsequently heating to 180° F. to 200° F. before separating the soapstock from the oil. The recommended temperature to which the mixture is raised prior to separation is, generally speaking, from about 160° F. to about 200° F. By using the higher mixing temperature, there is a decrease in the viscosity of the oil, resulting in smaller mist particles of oil in the mist-mixing process whereby a better contact between the oil and the refining agent is achieved so that

a better color is obtained than at lower temperatures.

In my aforementioned patent in the refining of crude oil, the broken emulsion is delivered to the centrifuge without delay in normal procedure. Particularly when a saponification-retardant is used, as in the present invention, a greater time element may be introduced between the reaction chamber and separating centrifuge.

Using the retardant, I have subjected the broken emulsion to agitation or turbulence for a period of a minute or two so that the following separation gives a refined oil without any free soapstock and with appreciable improvement in color. When the oil-soapstock mixture enters the refining centrifuge from the reaction chamber without delay, there are some particles of soapstock having a concentration of caustic on their surfaces such that the particles cannot fuse with the main body of the soapstock. By delaying the separation in the manner just mentioned, the concentration of the caustic on these soapstock particles is reduced by saponification of neutral oil thereby permitting the soapstock particles to fuse with the main body of the soapstock. Also, some additional color particles are removed.

When refining in accordance with the procedure given in my aforementioned patent, an 18% concentration of caustic soda is usually satisfactory in refining. However, when using a saponification-retardant, I have used as high as a 30% concentration of caustic soda. Usually a concentration of caustic soda of from 22% to 26% gives the best results, and I regard the practical limits as being from around 20% to around 30%. The soapstock obtained, while hard when cold, is fluid when hot. The fluidity of this soapstock, even when containing less water, is greater than the fluidity of soapstock not containing the retardant. I attribute this difference in fluidity to the difference in the amount of neutral oil in the two soapstocks. In the case of the soapstock not containing the retardant, the emulsion formed by the neutral oil stiffens the soapstock in the same manner that the emulsion known as mayonnaise dressing is stiff.

As stated above, using the retardant and subjecting the broken emulsion to agitation for a short period, I have been able to produce a refined oil containing substantially no free soapstock and this oil is otherwise perfectly clear as it leaves the refining centrifuge. In the absence of the said agitation, a slight cloud forms in the oil upon cooling, this cloud consisting of minute particles of soapstock which had been dissolved in the heated oil. While this soapstock in solution has been present in the refined oil produced by customary methods of refining, its presence has not been recognized because of the large amount of soapstock suspended in the refined oil.

I have discovered that by agitating the cooled oil, the minute particles of soapstock are caused to agglomerate so that the resulting larger particles can be removed from the oil by a clarifying centrifuge at a normal rate of through-put. The refined oil from the refining centrifuge can be continuously cooled to throw the soapstock out of solution and agitated to agglomerate the soapstock particles, and the agglomerated soapstock removed by a clarifying centrifuge without the necessity of washing and drying. The oil thus obtained contains less soap than that produced in the usual practice involving water washing and, of course, the process of removal is much simplified. One reason for the better result is that when the washing procedure is used, the wash water retained in the washed oil has to be evaporated with the result that the soap which was dissolved in the water becomes dissolved in the oil.

When the oil-soapstock mixture is subjected to proper agitation in advance of the refining centrifuge the cloud above mentioned will not form upon cooling, and the refined oil can be run directly to a clarifying centrifuge for the removal of any free soapstock. As a matter of fact, there is so little free soapstock, if any, in the oil having the refining centifuge that the subsequent clarification step could ordinarily be omitted, but to be on the safe side I ordinarily include the step.

The agitation prior to separation can be very effectively accomplished using a "Votator" which is a heat-transferring and agitating device manufactured by the Girdler Corporation of Louisville, Kentucky. In the "Votator" I, for best results, maintain the temperature of the oil-soapstock mixture and may even raise the temperature to any point desired. However, it is simpler to impart the desired temperature to the mixture entirely in the reaction chamber.

A probable explanation of the mechanism of the action of the use of the Votator between the reaction chamber and the refining centrifuge to prevent the formation of a cloud in the refined oil after the oil is separated from the soapstock is as follows:

At the temperatures used in refining glyceride oils, they have the ability to dissolve some water, which water in the refining operation has soap dissolved in it. Upon cooling the oil, some of this water is thrown out of solution as a cloud in the oil. This cloud is in reality a suspension of droplets of emulsion in the oil by reason of the emulsifying action of the soap in this water deposited from the oil in cooling. These droplets of emulsion do not coalesce readily. This is the condition which prevails when a Votator is not used between the reaction chamber and the refining centrifuge and the refined oil discharged from the refining centrifuge is cooled.

When a Votator is used between the reaction chamber and the refining centrifuge the water in solution in the oil is removed from the oil by the adsorptive effect of the water adsorptive retardant present in the soapstock. Since the water is only slightly soluble in the oil and the water adsorptive material has an affinity for water, the Votator by bringing the oil in intimate contact with the soapstock causes the oil to become dry. This dried oil on being separated from the soapstock will not have a cloud formed in it when cooled because of the absence of water.

It is obvious, therefore, that the described agitation of the oil-soapstock mixture in advance of the refining centrifuge, when using a saponification retardant in accordance with the present invention, brings about a number of very important results.

In the refining procedures hereinabove considered, the original refining of crude oil has been principally in mind. However, the present invention extends also to re-refining or retreatment for the purpose of color removal just as in my aforementioned patent. According to that patent, a very slight excess of the caustic solution is used in re-refining and the same slight excess is usable when a saponification-retardant is used in accordance with the present invention. In other words, the excess over that theoretically required

to neutralize the free fatty acids in the oil may be of the order of .05% or less with consumption of the excess to such an extent that upon separation only a trace will remain for the purpose of maintaining the pH.

The hydrous oxides and hydroxides hereinbefore mentioned function also as color adsorbents, as has been pointed out. In re-refining, these agents may be viewed from another standpoint, namely, that of their ability to electrically neutralize colloidal particles which escaped neutralization during original refining and are still electrically charged in the refined oil.

Under this contemplation, there may be added to the refined oil a highly dispersed negatively charged colloidal suspension made, for example, by adding approximately 1.4 parts of a 50% solution of sodium hydroxide (or an equivalent quantity of potassium hydroxide) to approximately 5 parts of a 4% solution of chromium acetate. As a result of the addition of the sodium hydroxide to the solution of the chromium salt, there is formed a highly dispersed colloidal suspension of chromic oxide and when, as in the example just given, a sufficient quantity of sodium hydroxide is used, the colloid will be negatively charged.

In the case, for example, of a 5.5% free fatty acid oil which has been preliminarily refined, a colloidal suspension of chromic oxide prepared in the manner described above may be added in the approximate proportion of 2½ parts of the colloidal suspension to 100 parts of the oil. The colloidal suspension is intimately mixed with the oil, preferably by mist-mixing. The mixing may be carried out at room or higher temperatures and the emulsion then broken with subsequent separation of the soapstock from the oil with the pH maintained up to separation.

By re-refining in this manner, I have obtained a refined oil with a substantially lower color and with substantially less refining loss than can be obtained by prior practices. For example, starting with a cottonseed oil having a free fatty acid content of 5.5%, I have obtained by means of preliminary refining and subsequent treatment with a highly dispersed negative colloids, an oil having a color of 35 yellow-10 red with a refining loss of 14%. Starting with the same oil and using the standard procedure now practiced in the art, an oil having a color of 35 yellow-18 red was produced with a 17% refining loss. It would be necessary to re-refine the 18 red oil at least twice to lower the color to 10 red and, in so doing, the total refining loss would reach a figure between approximately 21% and 23%.

Whether, in re-refining, a hydrous compound is used in the aspect of electrical neutralization or in the aspect of saponification-retardation, both properties of the compound are, of course, exercised. In the aspect of electrical neutralization and in the case, for example, of chromium oxide, in forming the oxide, it is only necessary to add sufficient caustic to the chromium salt to insure the formation of a negatively charged suspension and to insure the presence of at least a trace of the caustic at the time of separation, and separation may follow immediately after mixing. In the aspect of saponification-retardation, the caustic is used in amount somewhat in excess of that theoretically required for the neutralization of the free fatty acids and a delay is introduced to permit saponification of the neutral oil for the purpose of color removal. Of course, in this latter situation, the oxide is also exerting its effect of electrical neutralization and in both cases the water and color adsorptive effects of the oxide are realized.

In the original mist-mixing refining of crude oil, I ordinarily select the hydrous materials with sole reference to their capacity for water adsorption, this in view of the fact that the colloidal soapstock necessarily formed can be relied on for the neutralization of the charged particles.

Prior to my recognition of the effect of caustic adsorption by hydrous oxides and hydroxides, I had refined crude oil using such a substance on the basis of its capacity for electrical neutralization in conjunction with a sufficient amount of refining agent to neutralize the free fatty acids. As an example, 2½ parts of the colloidal suspension of chromic oxide described above, together with 0.4 part of 50% sodium hydroxide were added to 100 parts of a 0.8% free fatty acid oil. After mixing and separating, an oil having a color of 35 yellow-4.5 red was obtained with a refining loss of 4%. It will be seen that in the example just given the ratio of chromic oxide to the oil by weight was about the same as that of the colloidal silica in tests Nos. 1, 2 and 3 hereinbefore mentioned.

It will be understood that the ratio of alkali to salt in the colloidal suspension may be varied through a wide range, it being only necessary to have any amount of alkali greater than that which is theoretically necessary to react with the salt. The concentrations of the salt and alkali are likewise variable. Where the colloidal suspension is added to the oil, the amount which is used may vary but it has been found that if the concentration of the salt is increased, it is necessary to add a greater amount of the colloidal suspension to the oil. This is apparently due to a lessening of the dispersion of the colloidal suspension upon an increase in the concentration of the salt.

While the colloidal suspension may be formed before mixing it with the oil, from a practical standpoint, I prefer to form it in the oil. For example, the solution of chromium salt and caustic alkali may be added separately to the oil, with agitation and formation of the colloidal suspension in the oil. Or, and still better, the metallic compound may be directly dissolved in the oil, and then the alkaline agent may be added to the solution with intimate mixture therewith. In carrying out the last-mentioned procedure, the solution and the alkaline agent are preferably mist-mixed.

As examples of suitable metallic compounds soluble in animal and vegetable oils, the following may be given by way of example: trimethyl aluminum, diethyl aluminum, tridodecyl aluminum, tetramethyl tin, tetraethyl tin; in general, organic metallic compounds having the general formula RM where R represents the ethyl or methyl group and M represents the metal group; organic metal compounds of the chelate type, and inorganic compounds such as stannic chloride, titanium tetrachloride, and aluminum chloride. Examples of silicon compounds soluble in glyceride oils which will react with caustic alkali to form hydrous colloidal silica are: methyl silicate, trimethyl-ethoxy-silicon, hexamethoxy-disilicon, and (trimethoxy silicon) (triphenoxy silicon) oxide. In general, any compound soluble in the oil which will react

with an alkaline agent to form the oxide or hydroxide of the element may be used.

As an example of procedure, I added 0.343% of stannic chloride to dry refined cottonseed oil having a color of 35.0 yellow, 9.7 red, and a free acid content of 0.3% and subsequently treated the oil with agitation with 1.46% of 20% caustic soda solution, heating the mixture to 140° F. The resultant oil had a color of 35.0 yellow, 4.9 red. In general, the amount of alkali agent mixed with refined oil containing a salt in solution is preferably slightly more than is required to react with the salt and the free acid in the oil.

Some metallic compounds soluble in oil will be hydrolyzed by water, and, therefore, instead of using an alkali agent to produce the finely divided suspension from the metallic compound, water alone may be used where it is unnecessary to form a negative charge; for example, in cases in which merely an adsorptive action on the electrically neutral coloring matter is desired. Examples of glyceride oil-soluble metallic compounds hydrolyzed by water are stannic chloride and titanium tetrachloride. After the compound has been dissolved in the oil, with thorough distribution, water is intimately admixed, as by mist-mixing. The electrically charged coloring matter in the oil is not removable to any appreciable extent by adsorption, and consequently, when this is the matter, or some of it, desired to be removed, the negatively charged colloidal suspension should be used. Such a suspension has also the capacity of rendering the originally charged color particles electrically neutral and hence susceptible, as well as the originally neutral matter, of adsorption.

As stated at the outset, the present invention is applicable in the refining of glyceride oils for the purpose of removing free fatty acids and/or colloidal impurities. As vegetable oils other than cottonseed susceptible of treatment in accordance with the invention, I may mention peanut oil, soya bean oil, palm kernel oil, linseed oil, coconut oil, and sesame oil; and as animal oils, tallow, whale oil, menhaden oil, shark oil. These species are mentioned merely by way of example.

In the accompanying drawing, I have shown apparatus suitable for the practice of the present invention using mist-mixing.

Referring to the drawing, reference numeral 1 designates a tank for the oil to be refined or re-refined and, as shown, it is equipped with a temperature-conditioning coil 2 and with an agitator 3 driven from a belt 4. The coil may be used to heat the oil, if such heating is desired, and the agitator is useful, for example, when it is desired to mix some substance intimately with the oil.

A pipe 5 leads from the bottom of tank 1 through a valve 6 to a variable delivery pump 7 which is controllable by means of a hand wheel 8 on a panel 9. The output of the pump goes through a pipe 10, heat exchanger 11, and flow meter 12 to a pipe 13 which leads to means adapted to deliver the oil to a centrifugal atomizing and mixing head 13' mounted in a closed reaction chamber 14 and driven from a belt 15. The heat exchanger 11 may be used in place of the coil 2 to heat the oil to any desired temperature. The coil 2 is ordinarily used to heat the oil as an aid to the mixing of a treating substance therewith.

Reference numeral 16 designates a tank for the refining agent and is here shown as equipped with a temperature-conditioning coil 17 and with an agitator 18 driven from a belt 19. A pipe 20 leads from the bottom of tank 16 through a valve 21 to a variable delivery pump 22 which is controlled by a hand wheel 23 on the panel 9. The output of the pump goes through a pipe 24 to a metering device 25 and thence through a pipe 26 to a delivery means at the head 13'. Means for delivering the oil and refining agent to the head and the head construction are fully described in my aforementioned patent and also in my Patent No. 2,341,536 of February 15, 1944, so that repetition here is believed to be unnecessary. Moreover, it will be understood that the centrifugal atomizing and mixing head is referred to herein merely as the best means known to me for producing homogeneous mist-mixtures.

The reaction chamber 14 is laterally jacketed throughout for the circulation of a temperature-conditioning fluid which, in the present case, will be a heating medium lead to the jacket from any suitable source through a pipe 27 and leaving through an outlet pipe 28.

Chamber 14 has a bottom outlet pipe 29 which discharges into an upwardly open receiver 30 having a bottom outlet in connection with a pump 31 whose outlet is in connection with a pipe 32 leading to a valve 33. In one adjustment of the valve, the output of pump 31 is sent directly to a pipe 34 which delivers to a refining centrifuge 35. In another adjustment of valve 33 the pump output is delivered to an agitating and delaying device 36 and thence to the pipe 34 which delivers to the centrifuge. The device 36 may also be equipped for temperature-conditioning and may conveniently and effectively be constituted by the "Votator" above mentioned.

Centrifuge 35 has an oil outlet pipe or spout 37 through which refined oil can be delivered to a receiver 38, or by manipulation of a valve 39 the output can be diverted to a pipe 40. The receiver 38 has a bottom outlet in connection with a pump 41 whose outlet leads to a valve 42 to be directed by the latter either to a pipe 43 or to a heat transfer and agitating device 44, desirably a "Votator." The outlet of the device 44 is in connection by means of a pipe 45, in which is interposed a valve 46, with a valve 47 by means of which pipe 45 can be placed in connection with a delivery pipe 48 for a clarifying centrifuge 49.

Pipe 43 leads through a valve 50 to the top of a tank 51 equipped with a heat exchanging coil 52 and an agitator 53 driven from a belt 54. Tank 51 has a bottom outlet in connection with valve 47 through a pipe 55 and, when valve 47 is appropriately adjusted, tank 51 can drain into the clarifying centrifuge through the pipe 55. The clarifying centrifuge has an oil delivery pipe or spout 56.

In the practice of the invention, tank 1 contains crude oil and tank 16 contains the caustic solution and, in preferred practice, a water-adsorptive substance which is distributed throughout the caustic solution by the agitator 18. If mixing is to occur at room temperature, coils 2 and 17 and the heat exchanger 11 are inactive. However, if mixing is to occur at an elevated temperature, as I prefer to do and am enabled to do when using a saponification retardant, the oil is heated to the desired temperature using either the coil 2 or the heat exchanger 11, or both, and the refining agent may also be heated from the coil 17. The preheating is such, for example, as to bring the mixing temperature to from 110° F. to 160° F.

Valves 6 and 21 being opened and pumps 7 and 22 operating, the oil and refining solution can be delivered to the head 13' in exactly the desired

proportions by observing the flow meters 12 and 25 and adjusting the delivery of the pumps by means of the hand wheels 8 and 23. The substances delivered to the head 13' are instantaneously reduced to mists, i. e. aerosols, mixed, and projected radially as a homogeneous mist-mixture. The term "mist-mixing" as used herein covers the formation of separate mists or aerosols before mixing, or the merging of the substances as liquids prior to mixing as mists or aerosols. If merged, in the case of reactants the point of mergence should not be so far in advance of the head 13' as to permit major reaction of the substances to occur while they are still in liquid form since otherwise the disadvantages inherent in liquid-mixing refining will begin to appear. "Mist-mixing" applies to the above described procedure wherein the caustic alkali and water-adsorptive agent are mixed as liquids and the liquid mixture is then mist-mixed with the oil. There is an ultimate mist-mixture of all of the substances, although some of them were preliminarily mixed as liquids. By a "mist" or "aerosol" I mean dispersions of minute particles which are of approximately colloidal dimensions as in a mist or fog. I do not limit the terms to include only those systems which will remain in dispersion for a long period of time, but, on the contrary, I use the term to describe the character of the dispersion at the time it is formed. I am not concerned with the permanency or stability of the mists or aerosols since the mixing thereof can be accomplished in a fraction of a second.

If mixing has occurred at room temperature, the collecting walls of the chamber 14 need be heated only sufficiently so that the mist which collects thereon as a liquid emulsion will have an emulsion breaking temperature imparted thereto as it flows downwardly as a film or thin layer on the walls. The imparted temperature may be in the neighborhood of 140° F. but preferably will be higher, for example, 180° F. If mixing has occurred at a temperature as high as 160° F., chamber 14 need be heated only sufficiently to substantially maintain the mixing temperature, which is also a breaking temperature. However, even if a mixing temperature as high as 160° F. has been used, chamber 14 is preferably heated so as to further raise the temperature above the breaking temperature, for example, to form 160° F. to 200° F., the optimum range being from about 180° F. to about 200° F. and the optimum temperature being 180° F. or thereabout. Although mixing may have occurred at a temperature above the breaking temperature, the so-called emulsion nevertheless forms because, the heat being not extreme, and the saponification retarding agent being present, the caustic is not immediately consumed.

It is my opinion that the neutralization of the free fatty acids is completed before the mist-mixture reaches the walls of the reaction chamber. There is some saponification of neutral oil by the excess caustic during flow down the chamber walls and to the outlet pipe 29 and up to the time of separation.

With pipe 29 delivering to the receiver 30 and the pump 31 in operation, the broken emulsion can be sent directly to the refining centrifuge 35, when valve 33 is appropriately set. In this case, it frequently occurs that free soapstock will be observed in the discharge. As above stated, this free soapstock can be entirely eliminated, or nearly so, and the color somewhat improved if a greater time lag is interposed between the reaction chamber and centrifuge, particularly, if during this period, the oil-soapstock mixture is agitated, and when agitation is applied, no cloud will form in the refined oil upon cooling. Hence, I prefer to put the mixture through the device 36 and this device may also supply heat so as to maintain the temperature of the mixture. I have successfully used a coil in place of the "Votator," except as regards the elimination of the cloud, the time of flow through the coil being between one and two minutes.

When the "Votator" 36 or like agitating device is used, the refined oil can leave the refining centrifuge by way of pipe 40 to any desired destination, or it may go directly to the clarifying centrifuge, by-passing both device 44 and tank 50. To accomplish the latter effect, a pipe 57 connects pipe 43 just below valve 50 with pipe 45 just above valve 46 and includes a valve 58 adjacent pipe 43 and a valve 59 adjacent pipe 45. By adjusting valve 42 so as to connect pump 41 with pipe 43, closing valve 50, opening valves 58 and 59, closing valve 46, and adjusting valve 47 to connect pipes 45 and 48, the pump will deliver directly to the clarifying centrifuge.

In some cases, it may be desired to get the broken emulsion to the refining centrifuge with the least possible delay and agitation so as to prevent re-emulsification and in that case the pump 31 can be omitted or by-passed or the reaction chamber outlet pipe can be made to deliver by gravity directly to the centrifuge.

If clarification is to be carried out by prior methods, the output of the refining centrifuge can be directed through pipe 40 to any desired point of storage or treatment. However, cloud removal may be effected by the clarifying centrifuge when the oil is cooled and agitated in advance thereof.

To this end, valve 33 is adjusted to by-pass "Votator" 36 and the refining centrifuge is made to deliver to the receiver 38. Valves 42 and 47 being properly set, the refined oil will pass through the device 44 wherein it is cooled to a temperature preferably below 100° F. and subjected to agitation so that the soapstock which was dissolved in the heated oil is thrown out of solution and the soapstock particles coalesce so as to be readily separable from the oil by the clarifying centrifuge 49 at a normal rate of through-put.

Or, without changing the setting of valve 47, by adjusting valve 42, so as to connect pump 41 with pipe 43, tank 51 can be filled. The oil in the tank may be permitted to cool normally or cooling may be accelerated by circulating a cooling medium through the coil 52. After the oil has cooled sufficiently so that the dissolved soapstock is thrown out of solution, the agitator 53 is operated to cause the coalescence of the particles and thereafter valve 47 may be adjusted so as to connect pipes 48 and 55 for delivery of the oil to the clarifying centrifuge. In this connection, I may mention that a series of three tanks, such as are disclosed in my above-mentioned Patent No. 2,342,042, may be used with the arrangement such that while one tank is emptying, another is being filled and a third tank is standing full.

In the above description of the operation of the system shown in the drawing, the adsorbent was said to be mixed with the caustic alkali in the tank 16. However, the additive may be introduced independently of the caustic, if desired,

and by the use of a multi-fluid nozzle such as is disclosed in my aforementioned Patent No. 2,341,536.

It will be seen that the illustrated apparatus is capable of carrying out all procedures which have been discussed herein and with variation in accordance with the results desired. However, I believe I have made it clear that the method of the present invention is by no means limited with respect to apparatus. The invention extends to all procedures and apparatus within the definitions of the following claims.

I claim:

1. The process of refining a crude glyceride oil, which comprises mist-mixing the oil with a water-adsorptive agent selected from the group consisting of "sodium silicate," colloidal silica, and mixtures thereof, and with a caustic alkali solution whose concentration is substantially within the range of 20% to 30% and which acts to neutralize the free fatty acids present in the oil to form soapstock, collecting the mist mixture on a surface from which it flows as a mixture of liquid oil and soapstock, imparting to the oil-soapstock mixture a temperature substantially within the range of 160° to 200° F., agitating the mixture to bring the oil into intimate contact with the water-adsorptive agent present in the soapstock while maintaining the temperature of the mixture against substantial decline, and separating the soapstock from the oil, the caustic alkali being used in an amount in such excess of that necessary to neutralize the free fatty acids that some of the caustic alkali is present at the time of separation and said agent being used in an amount effective to substantially reduce the neutral oil retained by the soapstock and to retard the saponification of the neutral oil.

2. The process according to claim 1 wherein the soapstock is separated from the oil in a centrifuge and the excess caustic is present at the time of separation so that a two-layer soapstock forms in the centrifuge.

RALPH H. FASH.

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