Patented Apr. 2, 1946 2,397,874

UNITED STATES PATENT OFFICE

2,397,874

REFINING FATTY OILS

Katherine Lloyd, Chicago, and Havard L. Keil, Clarendon Hills, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois

No Drawing. Application March 23, 1940, Serial No. 325,784

10 Claims. (Cl. 195—3)

This invention relates to the refining of fatty oils and deals more particularly with processes in which the crude oils containing impurities including proteins are subjected to the action of proteolytic enzymes in the presence of water whereby the impurities are rendered insoluble in the oil and can be separated from it.

The crude fatty oils which occur in nature normally contain, in addition to triglycerides, a small amount of free fatty acids and other substances of a complex chemical nature, some of which are proteins. In order to utilize the oil in commercial processes as in the manufacture of foods or soap, it is first necessary to remove these other substances which in this discussion will be referred to as impurities. Without removal of such impurities the oil cannot be hydrogenated or bleached in a commercially successful way and is otherwise not suitable for use in commercial processes.

The method which has been in universal use for the removal of these impurities is the caustic alkali method wherein the caustic alkali reacts with the free fatty acids to form soaps and may possibly react with the impurities, the soaps and impurities being separated out and removed as "foots." By this method of oil refining the fatty acids are necessarily removed, and as a practical matter some glycerides are always removed in the foots; and these features result in a relatively high refining loss.

A method of refining the natural oils so as to enable their use in commercial processes without the removal of free fatty acids would be of great commercial importance, and its value would be further enhanced if such a method were effective to remove in the impurities substantially all those substances which act as hydrogenation inhibiting factors or bleach inhibiting factors in the later processing steps.

In the past various kinds of treatments have been suggested for the refining of oils without removal of the free fatty acids, but none of these suggested treatments have ever had any commercial significance. Some of the suggested processes consist of treatment with bacteria of one or another type such as in Ekhard Patent No. 2,172,531, and others have consisted of yeast treatment such as disclosed in Babcock Patent No. 156,404, and others, as in Ayres Patent No. 1,737,402, consist of treatment with water only. All of these have fallen short and have failed to displace the caustic alkali methods already in commercial use.

We have discovered processes which are effective in the removal of impurities from the oil without removal of free fatty acids. Furthermore our processes are effective to remove in the impurities those substances which are contained in the naturally occurring oils and fatty acids of such oils and which inhibit hydrogenation or bleaching action. Our improved methods depend upon the action of enzymes of the proteolytic type in causing the precipitation or flocculation of the impurities.

In carrying out the process we subject the crude oil to treatment with a small amount of a proteolytic enzyme, in the presence of water. Through the peculiar action of this enzyme the water and impurities combine, probably in a kind of hydration, to form insolubles. The insolubles may then be removed by centrifuging or by allowing the oil to stand until the insolubles have settled and then decanting the purified oil. We do not now know the exact mechanism by which this insoluble union is formed through action by the proteolytic enzyme. It is possible that the enzyme acts to sever certain protein bonds in the impurities to permit hydration of the impurities not before possible because of such bonds, or it is possible the proteins themselves being acted upon by the proteolytic enzyme hydrate and form about the other impurities to remove them from the oil. Also we do not now know whether the hydrogenation-inhibiting and the bleach-inhibiting factors removed by our improved process are themselves proteins or are removed only through the proteolytic enzyme action on the proteins. Evidently, the proteolytic enzymes do coact with the water in some way to convert the oil-soluble impurities into an oil-insoluble combination which can be separated off.

To be effective in our process the enzyme used must be a proteolytic enzyme; that is, it must be of a type having proteolytic activity. Papain, trypsin, pepsin, bromelin or ficin are examples of types which can be used. Various mixtures of such proteolytic enzymes may be used advantageously. These examples given are not intended as inclusive and any other enzymes or mixtures of enzymes having proteolytic activity may also be used. The proteolytic enzymes here referred to do not necessarily include all enzymes which act on proteins but do include those enzymes which hydrolyze or cleave the protein molecule. We have found that those enzymes without proteolytic activity are of no use in the practice of our invention and do not serve the desired function in our processes; for example, yeasts are ineffective, and the enzyme rennin, which is

chiefly a casein coagulant and does not have proteolytic activity, is altogether ineffective in our process.

Of the proteolytic type of enzymes which may be used we find papain particularly advantageous. We now believe that this can be explained by the fact that papain has proteolytic activity over a wide pH range, and since the pH of the oil is normally not the optimum for proteolytic action, papain is more effective to perform the desired function under the ordinary operating conditions of purification. We find also that the enzyme trypsin is very effectively used in our processes.

The amount of proteolytic enzyme necessary to perform the desired function is very small and is of the order of .002 to .01 per cent by weight of the oil being purified. In the case of papain only about 1 pound of the powdered enzyme material now marketed as having a proteolytic strength of 1:200 is required to thoroughly refine 30,000 pounds of oil. Of the other proteolytic enzymes which may be used in our method, we find that in general about the same amount or possibly a slightly larger proportion of enzyme is desirable.

Lesser amounts of the enzymes, of the order of 1 pound of enzyme material to 60,000 pounds of oil, may be used, depending on the character of the oil being treated, but if the amount is too greatly reduced the oil will be incompletely purified. Also greater amounts such as 2, 4, or 6 pounds of enzyme powder per 30,000 pounds of oil, may be used, but the additional amounts usually result in no substantial benefits; and if the amount used becomes too great, digestion of the proteins proceeds to a stage not desirable and this results in the impurities being again released and rendered soluble in the oil which defeats the purpose for which the enzymes are used. It will therefore be clear that our process involves not a proteolysis to the point of decomposition but only such action as enables or facilitates the formation of compounds insoluble in the oil.

Though our invention in its broadest aspects may be practiced using water in the amount of from as low as 1 or 2% of the oil up to 40 or 50% or even higher, we have further discovered that by limiting the amount of water employed we obtain an impurity compound of a different and improved character. We prefer to use around 4 or 5% of water but usually not exceeding 10%. When we use such limited amount of water the flocculent water-impurity formation is of a gelatinous nature, appears to cohere more effectively, and produces a cleaner separation from the body of the oil. Too, the agglomerated particles are relatively large in size when the water is limited, and will settle into a layer of lesser volume. To distinguish this oil-insoluble compound of improved character we will call it a gelatinous flocculation. It will be understood that by this term we do not mean the compound is necessarily stiff or like jelly, and in most cases it is of a soft gelatinous nature.

On the other hand when the amount of water is more than 20 per cent of the oil, the character of the flocculation is entirely different. In these cases the layer occupied by the compound after settling, is larger, and instead of being an agglomeration of fairly large particles of gelatinous nature, is composed of quite fine particles which appear to be somewhat suspended in the lower layer. After a longer settling period the impurity compound will finally form below or in the lower portion of the excess water, but such operation is less advantageous. The amount of water which it is best to use for obtaining the impurity compounds of improved character will vary somewhat depending on the oil purified and the amount of impurities contained in it, but having in mind the character of the impurity compound desired it is simple to adjust the specific quantity of water used to obtain this result.

Though as above stated we prefer to use a limited amount of water to produce the flocculation of improved character, we need not so limit the water used and can use larger amounts of water while still obtaining great advantage through the practice of the invention.

The temperature employed may follow somewhat the temperature at which the proteolytic enzyme used is more active, but we find that in the case of higher temperatures this principle does not hold, and that it is better to hold the operating temperatures in the range of between 100° to 110° F. For example, we find that in the purification of soya bean oil using papain, it is much better to employ temperatures between 100° to 110° F. though the temperature of greatest activity for papain is in the range of about 145° to 155° F. Indeed when the temperature is raised to about 115° F. we have noticed a very marked difference in the functioning of the enzyme to form the insoluble flocculation. When we are working with normally hard fats we must, of course, use temperatures sufficiently high to melt the fat reducing it to a liquid.

While as above stated we prefer to employ temperatures in the range of 100° to 110° F., temperatures outside this range result in effective operation. It will, of course, be recognized by those familiar with enzymes that the temperature employed should not be below that at which the enzymes have any activity and should not be above that at which they are destroyed.

Our process may be practiced by heating the oil in a large tank to a desired temperature such as 105° F., and then mixing into the oil the enzymes and water by mechanical agitation. Alternatively the enzyme and water may be added before the oil is heated, but this way a longer time is required for processing since the enzyme has very little proteolytic activity until the temperature is raised to about 90° F.

One good way of performing the treatment is to start a mechanical stirrer in the processing tank and apply heat, then when the operating temperature is reached add the water containing the enzyme, continuing the stirring to mix the water and enzyme with all parts of the oil. Another way is to first add the major portion of the water and then add an aqueous solution of the enzyme. Within usually about 10 minutes after the addition of the enzyme a "break" will occur, as evidenced by the presence of small masses which tend to collect within the oil, causing the oil to have a mottled appearance. These small collected masses are the product of the union of the water and impurities as created by the action of the proteolytic enzyme. This mottled effect then becomes more pronounced during the period of enzyme activity. Preferably stirring is stopped as soon as a satisfactory flocculation is obtained; this usually requires about 20 minutes. The oil can then be allowed to stand until the collected masses are separated out and lay on the bottom of the tank. Conveniently this is accomplished by allowing the oil to stand overnight. The purified oil is then drawn off and thus separated from the oil-insoluble substances. The losses may be further

reduced by stirring the insoluble mass which contains a certain amount of oil, and then allowing time for settling, after which a further quantity of purified oil can be drawn off.

We find it advantageous to employ the mechanical stirrer in mixing in the enzyme and water, and so far as possible to avoid beating air into the mass. Oxidation produced by the air is a chemical change which we find undesirable. Not only does oxidation adversely affect the character of the oil, but it also restricts or inhibits the full action of the proteolytic enzyme.

Instead of allowing the oil to stand until the insoluble floc has precipitated to the bottom, the oil may be passed through a centrifuge to separate the insoluble compound from the oil. This operation enables the oil to be refined in a shorter period of time.

Though the substances removed from the oil in our process have been designated as impurities, they are not to be understood as always being waste materials. Indeed, it has been discovered that this improved method presents a very effective way to recover lecithin from soya bean oil, and in many other instances the so-called impurities have valuable uses.

Our processes are applicable to any of the vegetable, animal, and marine oils such as soya bean, peanut, cocoanut, sardine and cottonseed oils and tallow and lard oils, but it is advantageous to vary the conditions in some instances depending on the oils being treated. In general the oils treated by our process can be hydrogenated and bleached by the usual processes applicable to oils refined by the caustic method and in most instances we have found that the hydrogenation or bleaching operations proceed with greater ease and speed than in the case of caustic refined oils. To our knowledge no other process, excepting the caustic refining method, has ever been known which would permit the ready hydrogenation or bleaching of the purified oil. By our method the free fatty acids remain in the oil and upon subjection to hydrogenation these free acids also take on hydrogen. In the past it has been thought that fatty acids occurring in oils inhibit the hydrogenation of the oils, but as demonstrated by our improved process, when the hydrogenation inhibiting substances are removed, not only will the purified triglycerides readily hydrogenate, but the fatty acids contained will themselves readily hydrogenate.

Soya bean oil is peculiarly susceptible to treatment by our improved processes, and it appears that the character of the impurities normally contained in the crude soya bean oil are particularly responsive to combination with water by influence of a proteolytic enzyme. When purified by our method, soya bean oil with its free fatty acids content will react with hydrogen much more readily than will oil refined by the caustic method and having its free fatty acids removed. The enzyme purified soya bean oil may also be easily bleached using only the common color-absorbing agents.

Though our process can be used to remove impurities from cottonseed oil we find that this oil when so purified may yet not bleach to the extent desired when using the ordinary absorption agents. This is believed to be due to certain bleach inhibiting substances contained in cottonseed oil which are not all removed by our enzyme treatment. In the case of cottonseed oil where it is desired to bleach the oil to obtain a very light color it may be desirable to use special bleaching agents. Alternatively the cottonseed oil after being treated by our process may be given a very light caustic wash to remove any color holding bodies which it may then contain before it is subjected to the ordinary bleaching agents.

The oils purified by this method and containing their free fatty acids may be steam-distilled and the free fatty acids removed in vaporous form and separately condensed. This procedure yields a highly purified triglyceride which may be especially suitable for edible purposes, and also a quantity of fatty acids which may be used in the manufacture of soaps or in other commercial processes. The possible uses of the relatively pure fatty acids recovered in this procedure are to be contrasted with the ineffective disposal of these acids in the caustic refining method where they are in chemically combined form with the impurity materials.

While our invention may be practiced without hydrogenation or bleaching of the refined oil, we find that by carrying on the process to include the steps of hydrogenation, bleaching, or steam distilling, special and advantageous results can be accomplished.

Another advantage gained through the use of the proteolytic enzyme treatment is that the refined oil, though it retains its fatty acid content, is more stable and develops rancidity less readily. This is noticeable especially in the case of soya bean oil which after alkali refining has a tendency to develop poor taste and odor. The oil purified according to our improved method remains "sweet" for a greater period of time.

Following are some examples of the practice of our invention to demonstrate specific ways of performing the steps involved:

Example 1

50,000 pounds of soya bean oil are agitated and heated to 113° F. in a refining tank. Approximately 2,500 pounds of water are then added to the oil and as the water flows into the oil a mixture of 2 pounds of papain in about 3 gallons of water is introduced. Agitation is continued for about 20 minutes at 110° F. and the oil then allowed to settle. 46,000 pounds of oil are pumped off, the foots allowed to drain and settle from which 1,600 pounds more oil can be recovered. The foots are again allowed to settle and further quantities of oil recovered therefrom. The total refining loss is under 2.5%.

Example 2

500 parts by weight of crude peanut oil are treated with 25 parts by weight of water and 0.018 parts by weight of commercial papain at 104° F. and the whole agitated for about one hour. The oil is then allowed to settle and the refining loss is 5.0%. The oil is bleached, using regular bleaching earth, from an original color of 35 yellow and 7.6 red (Lovibond) to 20 yellow and 3 red.

Example 3

1,000 parts by weight of crude cocoanut oil are treated at 104° F. with 0.1 part by weight of commercial papain in 50 parts by weight of water. After settling overnight there are 98 parts by weight of foots recovered, corresponding to a 4.8 percent refining loss. A comparative run, using caustic refining in the regular way, shows a 12.4 percent refining loss.

Example 4

To 500 parts by weight of crude cottonseed oil there is added with stirring 50 parts by weight of water containing 0.2 part by weight of trypsin assaying 1:40 by the U. S. Pharmacopoeia test. The temperature is maintained at 104° F. for about one hour and the oil then allowed to settle. A fine compact foots, dark and resinous in appearance, is obtained. The loss in this step is 0.55 percent. The oil recovered is rather dark in color but is clear and does not show any flocculation when heated to 250° C. A comparative test, but using no enzyme, gives a less compact foots and the oil recovered shows a considerable brown floc upon being heated to 250° C. A batch of cottonseed oil treated, according to Example 1, with papain in the proportion of 5 pounds of commercial papain to 60,000 pounds of oil gives an oil which, although not as light in color as would be desirable for some purposes, does not darken nor show a floc upon heating to 250° C.

Example 5

3,850 parts by weight of lard is heated to about 55° C. in order to melt the lard and there is then added 190 parts by weight of water containing 0.2 parts by weight of trypsin with continuous agitation. The mixture is held at 131° F. for about an hour, with stirring, and then allowed to settle. The oil is separated from the sludge and the refining loss is 1.57 percent.

While the examples given illustrate specific ways in which the invention may be practiced with respect to a few fatty oils, it will be apparent that the improved treatment is applicable to other oils as well, and that various changes and adjustments can be made in the operation and conduct of the processes without departing from the spirit of the invention.

We claim:

1. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water to produce from said proteins and water a gelatinous water-insoluble flocculation which is insoluble in said oil, and separating said oil-insoluble water-insoluble flocculation from the oil.

2. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of papain in the presence of water to produce from said proteins and water a gelatinous water-insoluble flocculation which is insoluble in said oil, and separating said oil-insoluble water-insoluble flocculation from the oil.

3. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of trypsin in the presence of water to produce from said water and trypsin a gelatinous water-insoluble flocculation which is insoluble in said oil, and separating said oil-insoluble water-insoluble flocculation from the oil.

4. A process for refining crude soya bean oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water to produce from said water and proteins a gelatinous water-insoluble flocculation which is insoluble in said oil, and separating said oil-insoluble water-insoluble flocculation from the oil.

5. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water in the amount of less than 10% of said oil to produce from said water and proteins a gelatinous water-insoluble flocculation which is insoluble in said oil, and separating said oil-insoluble water-insoluble flocculation from the oil.

6. A process for refining gatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water to produce from said water and proteins a protein substance in the form of a gelatinous flocculation insoluble in said oil and insoluble in water, and before proteolytic digestion has proceeded to render said substance water-soluble and while it is in the form of a gelatinous flocculation separating said substance from the oil.

7. In a process for refining fatty oil containing oil-insoluble proteins to obtain a refined oil substantially free of said proteins, the steps of bringing a hydrolyzing proteolytic enzyme and water into intimate admixture with said oil while agitating said oil while avoiding aeration thereof until said proteins are formed into a gelatinous flocculation and become oil-insoluble, and while said proteins remain in oil-insoluble water-insoluble flocculated form separating them from said oil.

8. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water at a temperature of from 100° to 110° F. to form a flocculate oil-insoluble water-insoluble protein-containing substance, and while said substance remains in flocculate oil-insoluble water-insoluble form separating it from the oil.

9. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water in an amount less than 10% of said oil to form a flocculate oil-insoluble water-insoluble protein-containing substance, maintaining said oil in a quiescent state until said substance has settled, and decanting the oil from said substance while said substance is in its oil-insoluble water-insoluble form.

10. A process for refining fatty oil containing oil-soluble proteins to obtain a refined oil substantially free of said proteins, comprising subjecting said oil to the action of a hydrolyzing proteolytic enzyme in the presence of water to form a flocculate oil-insoluble water-insoluble protein-containing substance, and before said substance has precipitated from said oil, and while said substance is water-insoluble passing said oil in rapid centrifugal motion to separate said substance from said oil.

KATHERINE LLOYD.
HAVARD L. KEIL.