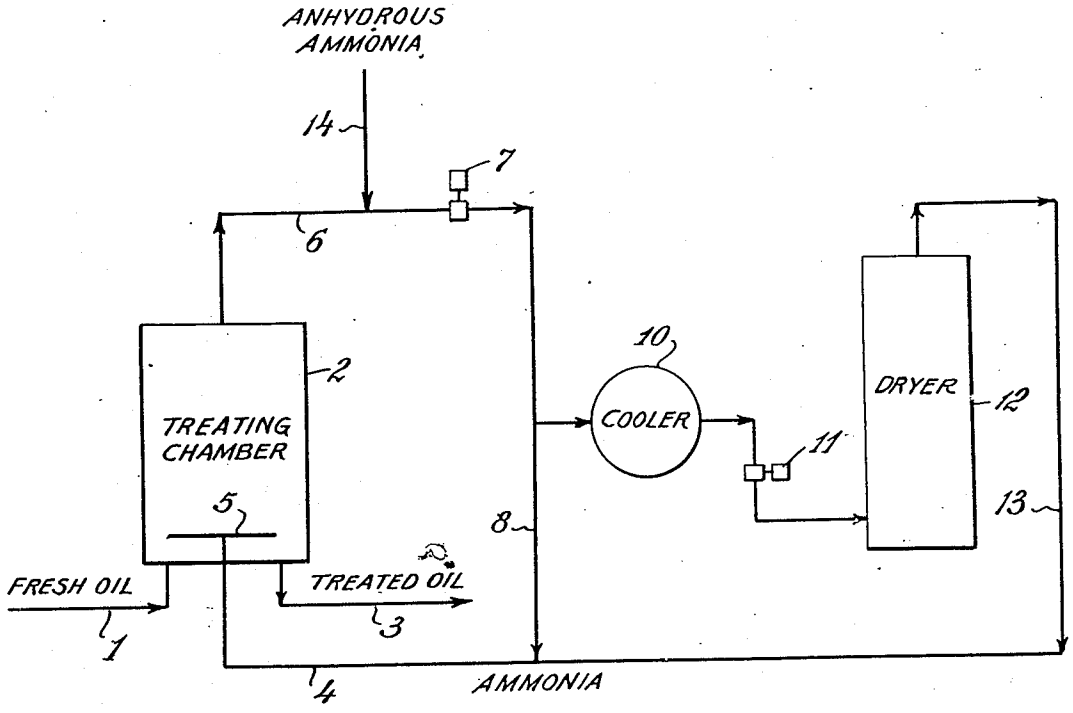
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REFINING OF OIL

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INVENTOR
FRANKLIN M. WATKINS

BY Pentlie, Davis, Marshall & Edmonds
ATTORNEYS

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REFINING OF OIL

Franklin M. Watkins, Chicago, Ill., assignor to Sinclair Refining Company, New York, N. Y., a corporation of Maine

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This invention relates to the treatment of petroleum hydrocarbons and, more particularly, to the refining of petroleum oils. The invention includes an improved method of decreasing the corrosiveness and of increasing the stability of petroleum oils as well as the production of improved oils resistant to oxidation.

Petroleum oils, and particularly those oils within the range of lubricating oils, contain a considerable quantity of organic acids and esters which impart corrosiveness to the oil and render the oil susceptible to oxidation with the resulting formation of sludge and similar deposits during storage and use. In order to reduce the corrosiveness of such oils and to improve their resistance to oxidation it is conventional practice to subject the oils to the action of caustic soda, or the like. Caustic soda reacts with the acids in the oil to form soaps, and the resulting soap and excess caustic is separated from the oil either by washing the mixture with water or by distilling the treated oil from the soap.

It has been found, heretofore, that many oils are not responsive to treatment with caustic soda. In the refining of such oils as can be treated in this manner, the caustic has a corrosive action upon iron and requires the use of special alloys for the equipment in which the oils are so treated with the caustic. Furthermore, difficulty is encountered in separating the soap and excess caustic from the oil after treatment thereof. Thus, when separation is effected by water washing the oil-soap mixture emulsions of oil and water are frequently formed, and long settling periods together with increased storage space are required to effect separation of oil and water layers from such emulsion. A further disadvantage arises from the fact that a large volume loss is realized during this washing operation. The minimum volume loss is that of the acids which are removed from the oil in the form of soaps, but actually an additional amount of oil is lost due to emulsification in the extracted water-soap mixture. In some instances, this mechanical loss of oil becomes so serious as to be of vital importance. When the separation of soap and excess caustic from the treated oil is effected by distillation of the oil rather than by washing, the residual oil which is not removed by distillation is contaminated with the soaps and excess caustic. These contaminants increase the amount of ash in the residual oil and thereby decrease the value of the residual oil or any products derived therefrom.

I have discovered that the requirement of special alloys equipment can be eliminated and that the other disadvantages inherent in the caustic alkali treatment of oils may be avoided by treating the oil with ammonia in lieu of the caustic alkali. I have found that when oils containing organic acids and esters are subjected to the action of ammonia these acids and esters are converted to nitriles. The nitriles thus produced in situ in the oil need not be removed from the oil and actually increase the oxidation resistance as well as the oiliness of the oil. In this manner the unstable products in an oil are converted to stable products which remain in the oil to improve its physical characteristics.

The organic acids and esters present in petroleum oils may be represented by the formulas RCOOH and RCOOR, respectively, in which R may be either an alkyl, cycloalkyl or aryl radical, or a mixture of these radicals. I have found that these organic acids and esters may be converted to nitriles by treatment with ammonia, water being formed as a reaction product during this conversion. I have found further that substantially anhydrous ammonia may be used with particular advantage in order to minimize the amount of water present during treatment. The presence of moisture interferes with the reaction so as to prevent formation of the nitriles. However, after these nitriles are produced within an oil they are not appreciably hydrolized by moisture. The conversion of acids and esters to corresponding nitriles can be effected by treatment with anhydrous ammonia at temperatures ranging between about 5000° to 730° F. Temperatures of about 530° to 650° F. may be used with particular advantage. The rate of reaction increases as the temperature increases so that the maximum temperature, particularly in the case of lubricating oils, is limited to the temperature at which the oils begin to crack. The extent to which the acids and esters are converted to nitriles is controlled at least in part by the length of time of contact between the oil and the ammonia at a particular treating temperature. I have found further that certain catalysts such as metallic oxides and salts having dehydrating characteristics will accelerate the conversion of both the acids and the esters so as to reduce the required time of oil-ammonia contact.

The amount of free organic acids contained in a petroleum oil is conventionally expressed as the "acid number" of the oil. This acid number is expressed in turn as the number of milligrams of potassium hydroxide required to neutralize a

gram of the oil. The amount of esters contained in petroleum oils is expressed as the "saponification number" of the oil, the saponification number being the number of milligrams of potassium hydroxide required completely to saponify the esters contained in one gram of the oil. Thus, a reduction in the acid and ester content of an oil is evidenced by a reduction of the acid number and saponification number of that oil. In practice, the specifications for lubricating oils for various purposes include limits for the allowable quantity of acids and esters which may be tolerated in such oils.

In carrying out the process of my invention a body of oil to be treated is maintained in a closed chamber and is heated to a temperature in the range approximating 500°–730° F. or better between 530° and 650° F. Anhydrous ammonia is introduced into the oil at the bottom of the chamber in the form of a plurality of fine streams so as to agitate the oil with a plurality of streams of small bubbles which pass upwardly through the body of oil. These bubbles provide a large interfacial area of contact between the oil and the ammonia. The ammonia is bubbled through the oil for a period of several hours until the acid and saponification numbers of the oil have been sufficiently reduced. At the end of this period the oil is cooled out of contact with air and may be treated subsequently in accordance with the usual refining methods for improving its color and other characteristics. The atmosphere of ammonia produced at the top of the chamber prevents oxidation of the heated oil, and excess ammonia is withdrawn for recycling through the body of oil. The recycled ammonia is dehydrated with advantage before being returned to the oil under treatment. In batch operations an inert atmosphere is maintained over the body of oil under treatment while the oil is being heated to the required temperature in order to prevent oxidation of the oil during this period. This non-oxidizing atmosphere may be provided by sweeping the upper portion of the chamber with nitrogen or by bubbling ammonia through the oil before the required reaction temperature is obtained. A similar precaution is taken with advantage during cooling of the treated oil. This precaution is unnecessary in a continuous operation in which fresh oil, either cold or preheated, is introduced into the body of oil under treatment, although the treated oil which is continuously withdrawn may be cooled with advantage in a non-oxidizing atmosphere.

Petroleum fractions substantially liquid at treating temperatures may be treated continuously in a process represented schematically in the drawing. In such a process preheated fresh oil such, for example, as a side stream from a fractionating tower is admitted through line 1 to the bottom of a treating chamber 2 and is continuously withdrawn after treatment through line 3. Substantially anhydrous ammonia is introduced through line 4 into the bottom of the treating chamber and is distributed through perforated pipe 5 in a plurality of fine streams which become small bubbles and rise through the oil to the top of the chamber. Ammonia collecting at the top of the chamber is withdrawn through line 6 and is recycled by pump 7 through line 8 into line 4 for reintroduction into the treating chamber. At least a portion of the ammonia, which may contain a small amount of moisture produced during the treatment, is withdrawn from the system, passed through cooler 10, and is then forced by means of pump 11 into a drier 12 in which the water formed during reaction in the treating chamber is absorbed. Anhydrous ammonia leaving the drier through line 13 is then returned to line 4 for reintroduction into the treating chamber. Fresh anhydrous ammonia may be introduced into the system through line 14 to replace the ammonia used in conversion of the acids and esters to nitriles.

The following description of a specific embodiment of my invention is directed to the treatment of a South Texas distilled oil substantially unresponsive to treatment with caustic soda. This oil had a gravity of 18.1 API, a viscosity of 157.3 seconds Saybolt at 210° F., a Conradson carbon content of 1.33, an acid number of 1.0, a saponification number of 3.0 and an ash content of 0.002. Equal amounts of the oil were subjected to batch treatment with anhydrous ammonia, the ammonia being passed through the oil in a stream of fine bubbles. One batch, designated "A," was treated with ammonia at a temperature of 550° F., and another batch, designated "B," was treated with ammonia at a temperature of 550° F. in the presence of a catalyst comprising levigated alumina, the mixture comprising 95% by weight of oil and 5% by weight of the catalyst. The chamber in which the oil was treated was swept with nitrogen during heating of the oil until the temperature of the oil reached 550° F., and a similar inert atmosphere was provided after treatment and during cooling of the oil. The effect of these two treatments on the acid number of the oil is shown in Table I.

Table I

Hours of treatment	Acid number	
	Batch A	Batch B
0	1.0	1.0
5		0.4
8	.35	
10		0.1
11		0.1
14	.20	

The saponification number of the product obtained upon treatment of batch A was 1.8, and the saponification number of the product obtained from batch B was 1.5. Each batch was then blended with 40% of a pale oil and treated in two successive operations with 5 lbs. and 33 lbs. per barrel, respectively, of 98% sulphuric acid, neutralized with soda ash, washed and then topped to remove the pale oil. Batch B was filtered to remove the catalyst. The final product of each batch had the characteristics shown in Table II.

	Batch A	Batch B
Vis., 210° F	129.9	124.2
Conradson carbon	.696	.500
Ash	.10	.002
Acid number	.037	.05
Saponification number	.30	.15

Table II

It will be seen from the foregoing tables that both the acid number and saponification number are markedly reduced by treating a lubricating oil with anhydrous ammonia at an elevated temperature. The extent to which the conversion of the organic acids and esters is accom-

plished is increased with an increase of contact time between the oil and ammonia. The contact time is materially shortened by the use of a catalyst, the catalyst being effective not only in the conversion of acids but also in the conversion of esters. The oil obtained by such treatment with ammonia contains the nitriles in solution, and the resulting product has been found to have a higher resistance to oxidation than the original untreated oil as determined by the Indiana sluding test. Further tests have also shown that the nitriles increase the oiliness of the resulting product so as to enhance the lubricating value of the oil. Accordingly, the quality of a given oil may be improved by converting at least a part of its acid and ester content to the corresponding nitriles or by converting substantially the entire acid and ester content of the oil to nitriles and subsequently blending the treated oil with more of the same oil or with a different oil. Furthermore, the treated oil may be subjected to hydrogenation in order to convert the nitriles to amines which have more pronounced antioxidant properties than the nitriles. A relatively small proportion of amides may be produced during formation of the nitriles due to the presence of a small amount of moisture in the ammonia or the oil under treatment, or both. Accordingly, the treated oil may contain a small amount of organic amides in addition to the organic nitriles produces from the organic acids and esters contained in the original oil.

While my invention has been described hereinabove with respect to the treatment of a lubricating oil, it must be understood that this treatment is applicable to lighter petroleum fractions as well. The treatment of these lighter fractions is essentially the same as treatment of the heavier fractions. Applied to such fractions, particularly those vaporizing at the reaction temperature under atmospheric pressure, the treatment may be modified to suppress such vaporization, by imposition of pressure, or to acommodate such vaporization by appropriate choice of apparatus. The required time of contact between a vaporized oil fraction and the anhydrous ammonia is in general shorter than that required in the treatment of oil in liquid phase inasmuch as the intimate contact between vaporized oil and ammonia promotes more complete and faster reaction between the components. In such case if a catalyst is used the treating chamber may contain with advantage a porous bed of catalyst suitable for vapor phase treatment.

The nitrilation operation of my invention may be effected with advantage in a distillation process by passing an excess of dry ammonia through the still in admixture with the hydrocarbon vapors. If steam is used in such a distillation process amides are formed rather than nitriles due to the tendency of the nitrilation reaction to be reversible with respect to the production of nitriles from an intermediate product such as the amides. In this event the acids and esters contained in the hydrocarbon vapors will be at least partially converted into a more stable form, namely, the amides, and, after being dehydrated, the hydrocarbon vapors may be treated subsequently with a small amount of anhydrous ammonia at an elevated temperature to effect nitrilation of the amides.

It will be seen, therefore, that the process of my invention fosters several economic improvements. The process eliminates volume loss concomitant with the conventional removal of unstable and corrosive components of an oil by actually converting these unstable components to stable products which remain in the oil. Furthermore, the process eliminates the necessity of using special corrosion-resistant apparatus which is required in the conventional treatment of oil with caustic alkali, and the process further eliminates the additional steps of removing reaction products and excess treating agents which have been necessary heretofore. The petroleum products obtained in accordance with the process of my invention are superior to those obtained heretofore inasmuch as the treated oils contain compounds capable of increasing the oxidation resistance of the oils. Moreover, if the process of my invention is used in treating oils which are to be used for lubricating purposes the treated oils are characterized by increased oiliness due to the presence of the nitriles produced in situ directly from the undesirable components of the original oils.

I claim:

1. An improved petroleum oil which comprises a petroleum oil containing a small proportion of organic nitriles formed in situ in the oil by conversion of the organic acids and esters contained in the original oil to nitriles by subjecting the oil to the action of substantially anhydrous ammonia at a temperature from about 500° F. to a temperature below that at which substantial cracking of the oil occurs.

2. An improved petroleum oil which comprises the oil obtained upon treatment of an organic acid-containing petroleum oil with substantially anhydrous ammonia at a temperature from about 500° F. to a temperature below that at which substantial cracking of the oil being treated occurs, the improved oil containing a small proportion of organic nitriles produced from the organic acids contained in the original oil.

3. In the refining of petroleum oils containing at least one corrosive compound of the group consisting of organic acids and esters, the improvement which comprises converting said corrosive compounds in the oil to nitriles by subjecting the oil to the action of substantially anhydrous ammonia at a temperature from about 500° F. to a temperature below that at which substantial cracking of the oil being treated occurs.

4. In the refining of petroleum oils containing at least one corrosive compound of the group consisting of organic acids and esters, the improvement which comprises converting said corrosive compounds in the oil to nitriles by subjecting the oil to the action of substantially anhydrous ammonia at a temperature of about 500° to 730° F.

5. In the refining of petroleum oils containing at least one corrosive compound of the group consisting of organic acids and esters, the improvement which comprises converting said corrosive compounds in the oil to nitriles by subjecting the oil to the action of substantially anhydrous ammonia at a temperature of about 530° to 650° F.

6. In the refining of petroleum oils containing at least one corrosive compound of the group consisting of organic acids and esters, the improvement which comprises converting said corrosive compounds in the oil to nitriles by continuously introducing the oil to be refined into a treating chamber and maintaining the oil therein at a temperature from about 500° F. to a temperature below that at which substantial

cracking of the oil being treated occurs, continuously introducing substantially anhydrous ammonia into the body of oil within the chamber, and continuously withdrawing treated oil containing said nitriles from the chamber.

7. In the refining of petroleum oils containing at least one corrosive compound of the group consisting of organic acids and esters, the improvement which comprises converting said corrosive compounds in the oil to nitriles by maintaining a body of the oil in a treating chamber at a temperature from about 500° F. to a temperature below that at which substantial cracking of the oil being treated occurs, introducing substantially anhydrous ammonia into the body of oil, withdrawing excess ammonia from the top of the chamber, removing moisture from at least a portion of the excess ammonia, and reintroducing the dehydrated ammonia into the body of oil.

8. In the refining of petroleum oils containing at least one corrosive compound of the group consisting of organic acids and esters, the improvement which comprises converting said corrosive compounds in the oils to nitriles by subjecting the oil to the action of substantially anhydrous ammonia at a temperature from about 500° F. to a temperature below that at which substantial cracking of the oil being treated occurs, and subsequently hydrogenating the nitriles to form the corresponding amines in situ within the oil.

FRANKLIN M. WATKINS.

CERTIFICATE OF CORRECTION.

Patent No. 2,302,281. November 17, 1942.

FRANKLIN M. WATKINS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 35, for "5000°" read --500°--; page 2, second column, line 69, strike out "Table II" and insert the same in line 60, as a heading to the table; page 3, first column, line 11, for "sluding test" read --sludging test--; line 31, for "produces" read --produced--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of January, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)