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PROCESS OF REFINING PETROLEUM OILS
TO PRODUCE WHITE OILSNorman E. Lemmon, Hammond, Ind., assignor
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poration of IndianaNo Drawing. Application January 22, 1937,
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10 Claims. (Cl. 196—40)

This invention relates to the refining of mineral oils and, in particular, to the refining of so-called white oils, medicinal oils, etc. White oils are chiefly characterized by the fact that they are substantially colorless and by the fact that they are treated with strong sulfuric acid they suffer only a very small loss by solution in the acid, for example less than 10%, and in the case of white oils of medicinal grade the acid and the oil are colored only a light brown shade, i. e., no black sludge is produced as in the case of ordinary mineral oils less highly refined.

In the manufacture of white oils the process almost universally used is the treatment of a petroleum oil and especially a petroleum distillate with large quantities of sulfuric acid until little further treating effect is obtained. In general, fuming sulfuric acid of about 104.5% H_2SO_4 equivalent is employed and the acid is customarily applied to the oil in portions or "dumps". Thus in preparing a medicinal white oil approximately 8 pounds of fuming acid is used per gallon of oil, applied in eight or more successive dumps, the sludge being settled and withdrawn after each dump. In this manner about 50% of the oil is destroyed and removed by the acid and the loss of oil may be greater or less, depending on the nature of the mineral oil stock employed, i. e., character of the crude petroleum from which it is derived.

After the acid treatment is completed, which may be determined by suitable laboratory tests, it is necessary to remove from the oil certain compounds derived from the acid which are preferentially oil soluble and do not separate with the acid sludge. These compounds may be termed sulfonic acids, although various other names have been applied to them, such as "mahogany acids". It is customary to remove these compounds in the form of their soaps by extracting with alcohol, methanol, etc. and ethyl alcohol of about 60% concentration is satisfactory. According to usual practice, the acids are first neutralized with caustic soda or other base, after which the resulting soaps are extracted with a single alcohol wash. The oil is then thoroughly steamed to remove alcohol and any low boiling hydrocarbons, diluents, etc. which it may contain and is then blown bright with air. The final treatment consists in filtering the oil through fuller's earth which adsorbs traces of malodorous substances which would be very objectionable in medicinal oil. The fuller's earth or clay likewise removes any finely divided suspended matter and completes the refining.

I have now discovered that great difficulty is encountered in producing white oils from certain types of crude petroleum stocks when employing the above described process. For example, I have discovered that the petroleum distillates derived

from "Kittrell" crude from Houston County, Texas, are not amenable to refining by the customary process, chiefly because of the peculiar character of the sulfonic acids and soaps produced on acid treating. I have found that it is substantially impossible to extract the sulfonic soaps from the acid treated oil with the customary 60% alcohol wash. In the refining of these oils, however, I have discovered that the unneutralized acids can be readily extracted.

I have also found that the extraction of the sulfonic soaps with alcohol is greatly impeded by the presence of sodium sulfate. In the case of certain oils it is extremely difficult to remove all the sulfuric acid in the last stage of the acid treating process and accordingly when the oil is subsequently neutralized a certain amount of contaminating sodium sulfate is present in the oil to thereafter interfere with the alcohol extraction of the sulfonic soaps. As an example of the deleterious effect of contaminating salts such as sodium hydroxide and sulfate, a sample of finished white oil was doped with 1.5% of sulfonic soap and 0.1% of NaOH. One wash with 15% by volume of 60% alcohol would only remove 13.4% of the soap present. However, on the second alcohol wash 53.3% of the soap was removed and on the third alcohol wash 20% of the soap was removed. When no caustic was present the soap came out completely with one alcohol wash. The addition of Na_2SO_4 likewise has the same action, rendering the soaps insoluble in the alcohol.

Having made these discoveries, I have devised the following process for refining white oils from crudes which produce difficultly extractable sulfonic soaps. After the completion of the acid treatment I first subject the unneutralized so-called "sour" oil to alcohol extraction, preferably with alcohol of about 60% concentration, and usually in the range of 55–70%. The amount of alcohol required for the sour oil wash is suitably about 13–30 gallons per 100 gallons of oil. The alcohol may be applied in two or more dumps if the acidity of the sour oil is high, for example over 10 mg. of NaOH equivalent per gram.

After removing the wash alcohol, the oil is then neutralized with a caustic soda solution and washed again with alcohol of about 60% concentration to remove an additional quantity of sulfonic soaps which is facilitated by the fact that the initial alcohol washing of the unneutralized oil removed contaminating sulfuric acid, thereby reducing the amount of sodium sulfate otherwise present in the neutralized oil. By this combination of steps I am able to reduce the ash content of the oil to a very low figure, approximately .05%. The ash content is a valuable indication of the amount of undesirable sulfonic soaps which are left dissolved in the oil. The following table

shows a comparison of the results obtained on alcohol washing acid treated white oil from Kittrell distillate. It will be observed that in test No. 1 the total amount of alcohol employed was only 39.6 volumes per 100 volumes of oil and an alcohol extract of 229 grams was removed, whereas in test No. 3 where the alcohol was applied to the neutralized oil in the conventional manner a total of 92.4 volumes of alcohol per 100 volumes of oil was required to remove about the same amount of extract and the finished oil contained about the same amount of ash as in the finished oil resulting from test No. 1. Test No. 2 was conducted with double the amount of alcohol in the sour washes and gave a negligible improvement in ash.

Test No. 4 was conducted with an oil containing less initial acidity, in which case it was found necessary to use only a single application of 13.2 volumes of alcohol per 100 volumes of oil on the sour oil followed with another equal amount of alcohol on the neutralized oil.

quent to alcohol washing, a suitable inhibitor of oxidation. The organic amines, such as tributyl and triamyl amine, are fairly satisfactory but may not be used in medicinal oils because of their undesirable odor, although triethanolamine may be used satisfactorily. I have found that the poly hydroxy aromatic compounds such as hydroquinone and catechol are quite effective, especially in the presence of a small amount of sodium hydroxide. Derivatives of poly hydroxy aromatic compounds may also be used, such as tertiary butyl catechol. I may also use aminophenols and substituted aminophenols such as metol and benzylaminophenol.

Inorganic alkalies, such as caustic soda, may also be used alone in low concentrations of the order of .01 to 0.1%. They appear to activate the natural inhibitors present in the oil whereas without the alkali, and in the presence of water, these natural inhibitors are not effective. The following data illustrate the deleterious effect of water and also the stabilizing effect of the in-

Alcohol washing of sour and neutral acid treated white oil stocks from Kittrell crude

Test number	Acidity of sour oil—mg. NaOH per gram	Charge, grams	Method of washing	Number of alcohol wash	Volume of 60 percent alcohol per 100 volumes of treated oil	Weight of reduced alcohol extract, grams	Washing yield, weight percent	Saybolt viscosity at 100° F. of washed oil	Percent ash
1	18.0	3000	Sour.....	1	13.2	73	97.6	-----	-----
			Do.....	2	13.2	146	92.7	-----	-----
			Neutral.....	3	13.2	10	92.3	329	0.052
			Total.....	(3)	39.6	229	92.3	-----	-----
2	18.0	3000	Sour.....	1	26.4	102	96.6	-----	-----
			Do.....	2	26.4	112	92.9	-----	-----
			Neutral.....	3	13.2	4	92.7	327	0.050
			Total.....	(3)	66.0	218	92.7	-----	-----
3	18.0	3000	Caustic.....	0	0	45.5	98.5	-----	-----
			Neutral.....	1	13.2	95.0	95.3	350	0.320
			Do.....	2	13.2	10.0	95.0	349	0.264
			Do.....	3	13.2	37.0	93.7	338	0.147
			Do.....	4	26.4	16.0	93.2	331	0.070
			Do.....	5	26.4	16.0	92.7	327	0.050
			Total.....	(5)	92.4	220.5	92.7	-----	-----
4	5.2	3000	Sour.....	1	13.2	188	93.7	-----	-----
			Neutral.....	2	13.2	4	93.6	327	0.050
			Total.....	(2)	26.4	192	93.6	-----	-----

When refining white oils by my method of initially extracting the sour oil and subsequently neutralizing and extracting a second time, I have encountered difficulty with instability of the resulting product with respect to atmospheric oxidation. This difficulty appears to be caused by the removal of natural oxidation inhibitors present in the oil which appears to be more complete in the case of oil subjected to repeated extraction. As a result of this instability, the product rapidly oxidizes, especially during the subsequent air blowing operation necessary to remove moisture from the oil before the final treatment with fuller's earth, and the difficulty is greatest in the presence of water. Oxidation of this character produces in the oil certain malodorous compounds which appear to be chiefly organic peroxides characterized by their rancid odor. These peroxides may be quantitatively determined by titrating the oil with ferrous sulfate, using ammonium thiocyanate as an indicator and expressing the peroxide content in parts of iron per million in accordance with the method of Yule and Wilson, Journal of Industrial and Engineering Chemistry, 1931, page 1254.

I have discovered that this oxidation difficulty may be corrected by adding to the oil, subse-

hibitor. The oil was tested by heating with air at 210° F.

Stability tests on acid treated white oil (alcohol extracted sour, neutralized, alcohol extracted again and finally blown free of alcohol with air)

	24 hrs. aging at 210° F.	
	Peroxide number	Odor
Oil #1 blank—dry	None	None
Oil #1+5% H ₂ O	100	Bad
Oil #1+5% H ₂ O+0.008% NaOH	100	Trace
Oil #1+5% H ₂ O+0.02% NaOH	10	None
Oil #1+5% H ₂ O+0.008% NaOH+1 pt. TBC/M* ..	10	None
Oil #1+5% H ₂ O+0.02% NaOH+1 pt. TBC/M ..	10	None

	16 hrs. aging at 210°		40 hrs. aging—210°	
	Peroxide number	Odor	Peroxide number	Odor
Oil #2—blank+5% water	100	Bad	-----	Bad
Oil #2+1 pt. TBC/M (dry)	0	None	0	None
Oil #2+1 pt. TBC/M+5% H ₂ O	10	None	100	None
Oil #2+2 pt. TBC/M+5% H ₂ O	0	None	0	None

* 1 part of tertiary butyl catechol per million.

In applying the inhibitor in my process of refining white oils I treat a distillate of about 650 Saybolt viscosity (100° F.) with about 8 pounds of fuming acid per gallon as previously described and then after separating the sludge I wash the sour oil with 60% ethyl alcohol, using about 25-30% by volume of alcohol in one or two dumps. The oil is then neutralized with caustic soda and washed again with 60% alcohol, using about 10-20% alcohol by volume. This washing treatment removes substantially all the sulfonic compounds. I may then treat the oil with about .02% of sodium hydroxide and 1 part of tertiary butyl catechol per million parts of oil. The alcohol is then removed from the oil by steaming, after which the oil is blown bright with air, keeping the temperature of the oil at about 180-220° F. during the air blowing operation. The oil is then percolated through Attapulugus clay which has been dried at about 500-600° F. The clay effectively removes the tertiary butyl catechol and NaOH, a percolation yield of 1800-2000 gallons per ton being obtained. The finished oil has a viscosity of about 305 to 320 seconds Saybolt (100° F.). It is preferred to employ a wax-free distillate so that no dewaxing is required in the process. Naphthenic type distillates such as those from Kittrell crude are sufficiently free from wax.

Where the inhibitor is not used preceding the percolation and during the air blowing operation the yield of acceptable oil from the clay is very greatly reduced and it appears that the yield of satisfactory oil obtained in the clay treatment is greatly affected by the peroxide content of the oil before percolation. Thus where no inhibitor is used during the air blowing operation the clay yield may be reduced to 100 gallons per ton. It is therefore desirable that the unpercolated stock be substantially free of peroxides if satisfactory percolation yields are to be obtained.

The oil prepared by my method has been found to be quite stable on storage, as indicated by an oxidation stability test in which the oil is heated at 210° F. After 72 hours the peroxide content of the oil was less than 5 parts/million and the odor was not detectable. The stability may be still further increased by adding additional amounts of antioxidant to the oil after percolation, and tertiary butyl catechol in a concentration of 1 part per million may be used for this purpose.

Having thus described my invention, what I claim is:

1. In the process of refining petroleum oils to produce white oils by exhaustive treatment with fuming sulfuric acid wherein the acid treated oil contains sulfonic acids whose soaps are difficultly removable by alcohol washing, the improvement comprising washing said acid treated oils with alcohol before neutralization until a major portion of the sulfonic acids is removed, subsequently neutralizing the oil with alkali and then extracting substantially all of the remaining sulfonic compounds by further alcohol washing, removing the alcohol from the oil and finishing the oil by contacting with fuller's earth.

2. The process of claim 1 wherein the alcohol is finally removed from the oil by steaming and the oil is dried by air blowing in the presence of an oxidation inhibitor before contacting with fuller's earth.

3. The process of claim 1 wherein the alcohol is finally removed from the oil by steaming and

the oil is dried by air blowing in the presence of an alkali and an oxidation inhibitor before contacting with fuller's earth.

4. The process of claim 1 wherein the alcohol is finally removed from the oil by steaming and the oil is dried by air blowing in the presence of an alkali and an oxidation inhibitor comprising tertiary butyl catechol before contacting with fuller's earth.

5. In the process of refining petroleum oils for the production of white oils wherein a petroleum oil distillate is subjected to exhaustive treating with concentrated sulfuric acid and the resulting oil is neutralized with caustic soda whereby sulfonic acid and residual sulfuric acid are converted to sulfonic soaps and sodium sulfate, respectively, after which the oil is freed of sulfonic compounds by extraction with an alcohol selected from the class consisting of ethyl alcohol and methanol, the improvement comprising removing substantially all of the contaminating sulfuric acid from the oil after the final acid treatment and before neutralization, by extracting with said alcohol and thereafter neutralizing the oil and further extracting sulfonic soaps therefrom by said alcohol in the absence of sodium sulfate.

6. The process of claim 5 wherein the said alcohol is ethyl alcohol of 55-70% concentration.

7. In the process of refining petroleum oils to produce white oils by exhaustive treatment with fuming sulfuric acid, wherein the treated oil contains sulfonic acid whose soaps require two or more alcohol washes for their removal, dissolved alcohol is recovered from the oil by steaming and the oil is dried by blowing with air, the improvement comprising adding an alkali and an oxidation inhibitor to the oil after steaming and before blowing free of water.

8. In the process of refining white oils wherein a suitable petroleum distillate is treated with at least four pounds per gallon of fuming sulfuric acid, the acid sludge is separated and the oil is repeatedly extracted with alcohol to remove sulfonic compounds, the alcohol is removed by steam and the oil is dried by air blowing and finally finished by contacting with fuller's earth, the improvement comprising avoiding oxidation of the oil during the said air blowing operation with consequent reduction in the fuller's earth treating yield, by reducing the amount of alcohol employed in said extraction step and by air blowing the oil in the presence of a trace of caustic alkali, said reduction in alcohol extraction being accomplished by initially extracting the major part of the said sulfonic compounds in the acid condition and subsequently completely neutralizing the oil and completing the alcoholic extraction while the oil is in the neutral condition.

9. In the process of refining petroleum oils to produce white oils by treatment with fuming sulfuric acid, wherein the treated oil contains sulfonic acid whose soaps require two or more alcohol washes for their removal and the oil is steamed after alcohol washing to remove the alcohol therefrom, after which the heated oil is blown with air to remove water, the improvement comprising adding an alkali and an oxidation inhibitor to the oil both before and after the steaming operation.

10. In the process of manufacturing white medicinal oils from petroleum oil distillates wherein the distillate is exhaustively treated with fuming sulfuric acid resulting in the formation of sulfonic acid compounds which remain

5 dissolved in the oil and which require repeated extraction with alcohol for their removal, as a result of which naturally present protective oxidation inhibitors are also removed from the oil, the improvement comprising extracting the said sulfonic compounds with at least two alcohol

extractions, recovering the dissolved alcohol from the oil by steaming, then restoring an oxidation inhibitor to the oil, blowing with air to remove dispersed water and finally finishing the oil by filtering through fuller's earth.

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