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REMOVAL OF WAX FROM HYDROCARBON OIL

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This invention relates to the dewaxing of wax-bearing oil, and particularly to the separation of wax from a mineral lubricating oil.

The invention contemplates the separation of wax from such a wax-bearing oil by the employment of a wax crystal modifying material to facilitate dewaxing by filtration, centrifuging or cold settling. The use of various crystal modifiers in dewaxing processes employing a diluting or dewaxing solvent has heretofore been suggested. In commercial dewaxing plants employing dewaxing solvents, it is found difficult if not economically impossible to maintain the solvent of the system in an anhydrous condition, the solvent frequently containing as much as ½% or more of water. It is found that the majority of dewaxing aids or wax crystal modifiers heretofore proposed, such for example as the metallic soaps of the character of aluminum stearate, the polyhydric alcohol esters and analogous materials, lose their effectiveness in the presence of wet solvent. Moreover, due to hydrolysis in the presence of the wet solvent, such aids result in objectionably raising the saponification number and the neutralization number of the dewaxed oil. Other dewaxing aids of the character of asphaltenes, petroleum residuums, coal tar fractions and the like cause an objectionable discoloration of a pale oil being dewaxed. Where a mineral lubricating oil is being both solvent refined and dewaxed, the objections due to discoloration and rise in neutralization and saponification numbers can be in large part overcome by an order of steps in which the dewaxing precedes the solvent refining operation, the oil being finished by clay contacting. However, this order of steps is uneconomical in most operations because it means that a larger quantity of oil must be handled in the dewaxing step which precedes the solvent refining step, and in general solvent dewaxing is more expensive than solvent refining. It is therefore generally preferable to solvent refine prior to the solvent dewaxing step.

It is an object of the present invention to provide a wax crystal modifying material to facilitate dewaxing which is of such character that it retains high effectiveness in the presence of wet solvent, does not objectionably increase the saponification and neutralization numbers of the dewaxed oil, does not discolor a pale oil, and does not otherwise objectionably alter the desired characteristics of the dewaxed oil.

It is a further object of the invention to provide a dewaxing aid of this character which can be effectively recovered and reused so as to render the process commercially economical.

Further objects and advantages of the invention will be apparent from the following description and the appended claims.

In accordance with the present invention, there is used as a wax crystal modifying material a resinous material which is a reaction product of rubber with a compound selected from the group consisting of halides of tin and boron, and halogen acids of tin and boron. The particular type of resin contemplated herein is that produced when anhydrous solutions of rubber are treated with halide salts of amphoteric metals possessing residual or so-called secondary valences, such as stannic chloride or bromide, and boron trichloride, and the like, or when solid rubber is worked on a rubber mill with the same compounds, as described in U. S. patent to Bruson, No. 1,846,247; or when boron fluoride or fluorboric acid, produced as the reaction product of hydrofluoric acid with boric acid or metal salts of boric acid, are added directly to rubber and worked on a rubber mill at elevated temperatures to yield thermoplastic, moldable conversion products, or when the reaction product is added to a solution of rubber in benzene or other rubber solvent, as described in U. S. patent to Bruson, No. 1,853,334; or when halogenated acids of tin, such as chorostannic acid or chlorostannous acid or the corresponding brom-acids, are reacted with rubber, as by addition of approximately 10% of the reagent to rubber on a rubber mill, or to a solution of rubber in benzene or other rubber solvent, as described in U. S. patent to Bruson, No. 1,797,118. Specifically, the moldable thermoplastic resin which is now commercialized by the Goodyear Tire and Rubber Company under the trade name "Plioform" constitutes a very satisfactory material of this character. This resin veries in character from a balata-like substance to an exceedingly hard material resembling ebonite depending upon the reagents and proportions thereof employed. The characteristics of resins of this character are described by Theis and Clifford in J. I. E. C. 26, 123. The products contain a certain

amount of bound chlorine or halogen, depending upon the temperature and the proportions of the ingredients. They are soluble in benzene or other rubber solvents. They are softened upon the application of heat and may be molded. Typical properties of the resin have been determined as follows:

Specific gravity	1.06
Odor	None
Taste	None
Softening point, °F.:	
No. 20 Plioform	220
No. 40 Plioform	175–195
Molding temperature, °F.:	
No. 20 Plioform	310
No. 40 Plioform	260
Coefficient of thermal expansion	0.00008
Resistance to discoloration by light	Good
Surface resistivity (ohms per linear in.):	
At 90% relative humidity	1×10^{11}
At 75% relative humidity	1×10^{12}
Tensile strength, lb./sq. in	4000–5000
Compressive strength, lb./sq. in	8500–11000
Flexural strength, lb./sq. in	7000–9000
Water absorption (24-hr. immersion) per cent	0.03
Resistance to concentrated acid	Good
Resistance to strong alkali	Good

A purified type of resinous product formed by reacting rubber with one of the compounds specified above and then purifying the product, may also be employed in accordance with our invention. For example, it is found that the so-called "Plioform" type of resin may be not entirely oil soluble; in other words, it will dissolve in mineral oil to produce a hazy solution. While this is generally unobjectionable for dewaxing work where the material is used as a dewaxing aid, and in which it is largely precipitated along with the slack wax and separated from the dewaxed oil along with the slack wax, it may be of advantage in certain instances to utilize a purified product. This may be accomplished by forming a solution of the resinous material in an aromatic solvent of the character of benzol, and then filtering the solution through a solid adsorbent of the character of diatomaceous earth or other decolorizing clay. The filtrate constitutes a benzol solution of purified oil soluble product. The filtration may be conducted at an elevated temperature of the order of 100° F. more or less.

While in the method specified above for the so-called "Plioform" resin, a milling operation of the rubber on a rubber mill is generally used, this expensive processing may be avoided and a satisfactory product obtained by simply reacting a solution of rubber in a suitable aromatic solvent of the character of benzol in the presence of one of the group of compounds specified above, and then following this operation with a suitable purifying treatment such as discussed immediately above. An alternative procedure of purifying the resinous product comprises forming a solution of the product in a suitable aromatic solvent, such as benzol, then precipitating undesirable material from the solution by the addition of a mineral acid or glacial acetic acid, filtering off the precipitated material which consists largely of the oil insoluble portion which produces the haze, and then precipitating the desired resin by addition of a solvent of the character of a ketone or alcohol, such as acetone or ethyl alcohol.

Another very satisfactory resinous product for purposes of our invention is that produced in accordance with the co-pending application of Charles C. Towne, Serial No. 70,402, filed March 23, 1936. In accordance with that application, rubber in dispersion in a suitable aromatic solvent, such as benzol, is treated with a depolymerizing agent. This is accomplished by allowing the rubber dispersion to stand for a period of time, generally about twenty-four hours, in the presence of such a depolymerizing agent. Examples of suitable depolymerizing agents for this purpose are glacial acetic acid, hydrochloric acid, chloracetic acid, sulfur dioxide, hydrogen sulfide, benzoic acid, mercurous chloride and ammonia. The result of this treatment is to modify the rubber, giving a product of lower molecular weight and consequently termed "depolymerized".

The dispersion of depolymerized rubber is then treated with one of a group of compounds consisting of halides and halogen acids of tin and boron, such as stannic chloride or bromide, boron trichloride, boron fluoride, fluorboric acid, chlorostannic acid, chlorostannous acid, and the corresponding bromine acids. Anhydrous stannic chloride is preferred for this purpose. The reaction takes place by standing at room temperature for a period of time, such as about twenty-four hours. The resulting resinous product is then precipitated by admixing with a suitable precipitating solvent such as an alcohol or a ketone. For example, very satisfactory results are secured with 95% ethyl alcohol, acetone containing about 5% water, and methyl alcohol containing about 5% water. The precipitate is then filtered, washed free of acid with additional precipitating solvent, and dried.

In place of first adding the depolymerizing agent and allowing the mix to stand for the depolymerizing action, and then allowing the depolymerized material to react with the mentioned halides or halogen acids, it is found that equally good results may be secured in a shorter period of time by adding the depolymerizing agent and the mentioned halide or halogen acid simultaneously to the rubber dispersion and allowing the material to stand at room temperature for a period of about twenty-four hours. Apparently the depolymerizing agent first reacts to break down the rubber molecule, and then the depolymerized rubber reacts with the halide or halogen acid to produce the desired resinous product. As a specific example of forming a resinous material of this character, 50 grams of crepe rubber dispersed in 150 cc. of benzol (90%) are mixed with 15 cc. of glacial acetic acid and 10 cc. of anhydrous fuming stannic chloride. The mixture is allowed to stand twenty-four hours at room temperature. The product is then run into 3500 cc. of 95% ethyl alcohol, which effects precipitation of the resinous material. The precipitation is completed by stirring for two or three hours. The precipitated material is then filtered off, washed free of acid with alcohol, and dried. A yield of 96% by weight of resinous product based on the weight of the rubber used was obtained in the above example.

The resinous product produced as described above is a white powdery material which is very light in weight. It is substantially completely soluble in a mineral lubricating oil in proportions up to about 40% by weight. It possesses unusual viscosity index increasing properties, so that the addition of about 2%–3% of the product to a

mineral lubricating oil serves to increase the viscosity index thereof very materially.

It is found that the proportion of depolymerizing agent employed has an effect upon the yield of the soluble product. For example, where no glacial acetic acid is employed, about 50% of the resulting precipitate is insoluble in lubricating oil. Where 5 cc. of acetic acid is employed with the above mentioned proportions, a substantial quantity of insoluble product is still produced, although the yield of precipitate is substantially 100% on the weight of the rubber used. Where larger quantities of glacial acetic acid than 15 cc. for the above mentioned proportions of other ingredients are employed the entire precipitate is oil soluble and there is no apparent advantage in the use of the larger proportions. Consequently, for most economical production of oil soluble product, it is desirable to predetermine the proportion of depolymerizing agent employed so as to render the entire precipitate substantially completely oil soluble.

While it is of advantage frequently to employ the oil soluble product produced as outlined above, it is to be understood that the simple partially oil soluble product produced by the treatment of a dispersion of rubber in an aromatic solvent with one of the group of mentioned halides or halogen acids, may be employed as a dewaxing aid in accordance with our invention.

In accordance with the present invention, the wax crystal modifying material is added to a wax-bearing oil, and the oil then chilled with resultant precipitation of wax in a form which is found to facilitate separation by centrifuging or cold settling, and is also found to materially increase filtration rates where the wax is separated by filtration. The use of the dewaxing aid gives an improved yield of dewaxed oil, a denser or more compact wax cake, a higher percentage of paraffin in the slack wax, and other advantageous results. The resinous product as described above is preferably employed in conjunction with a dewaxing solvent or solvent mixture. Various solvents can be used for this purpose, including the well-known and conventional dewaxing solvents and solvent mixtures. Very satisfactory results are secured by the use of a mixture of a wax anti-solvent and an oil solvent, such as a mixture of acetone and benzol, methyl ethyl ketone and benzol, methyl ethyl ketone and isopropyl ether, acetone with benzol and toluol, and the like. In the case of methyl ethyl ketone-benzol or methyl ethyl ketone-isopropyl ether, generally a proportion of about 40–60% methyl ethyl ketone to 60–40% benzol or isopropyl ether is satisfactory.

The oil to be dewaxed is diluted with the dewaxing solvent or solvent mixture generally in the dilution ratio of about two parts of solvent to one of oil up to about four or five parts of solvent to one of oil, although a smaller dilution ratio may be employed in certain instances. The resinous product is added and dissolved in the diluted oil in order to give a proportion of about 0.1% to 1.0% on the weight of the oil. A proportion of about 0.4% has been found to be optimum for the particular stocks being dewaxed. The resinous product may be added as a solid and dissolved in the oil, but preferably the product is added in solution in benzol. For example, in manufacturing the resinous material, a solution in benzol may be obtained, and this can be conveniently employed without resorting to reducing the material to a dried solid. This is particularly convenient where a dewaxing solvent mixture containing benzol as the oil solvent is employed, inasmuch as the benzol accompanying the resinous material may then be utilized to bring up the solvent composition to the desired proportions of methyl ethyl ketone or other wax anti-solvent relative to benzol.

In a preferred procedure, the diluted wax-bearing oil containing the dewaxing aid is then heated to a super-solution temperature, or to a temperature substantially above the temperature of complete solution of oil in solvent, the latter being generally about 120–140° F. Thus, the mix is generally heated to a temperature of about 160–190° F. or to a temperature approximately 20–70° F. above the temperature of complete solution of oil in solvent. This is found to uniformly give improved filtration rates and yields of dewaxed oil. The mix is then chilled to a dewaxing temperature of the order of —10 to —15° F., and the precipitated wax separated from the oil. This is preferably accomplished by filtration, such as on continuous rotary filters, although intermittent pressure filters may be used with advantageous results. It is found that the bulk of the resinous material precipitates along with the wax and remains in the slack wax upon separation from the filtrate oil. The dewaxed oil is then stripped to remove the solvent, and the recovered solvent is recycled for the dewaxing of additional oil.

By way of example of the effectiveness of the resinous product of the present invention as a dewaxing aid, the following results were obtained in the dewaxing of a furfural refined acid treated Mid-Continent wax distillate with 40% methyl ethyl ketone and 60% benzol, the solvent containing approximately ½% water, in which a dilution ratio of four parts of solvent to one of oil was used, and where the wax-bearing oil mix was heated to a super-solution temperature of 170° F. and then chilled to a filtration temperature of —15° F. and filtered:

Dewaxing aid	Percent aid	Filter time (sec.)	Percent yield of wax-free oil
Blank	None	53	51.8
Plioform No. 40	0.5	7	80.0
Plioform No. 20	0.5	9	78.2
Do	0.5	5	77.2
Do	0.4	18	77.2
Do	0.3	14	75.4
Do	0.2	13	72.7

As illustrative of improved results employing the resinous product obtained by depolymerizing rubber and reacting with the mentioned halides and halogen acids, the following results of tests are listed:

Dewaxing aid	Percent aid	Filter time (sec.)	Percent yield of wax-free oil
Blank	None	53	51.8
Resinous product from depolymerized rubber	0.5	6	77.2
Do	0.4	11	78.2
Do	0.3	10	74.5

In order to improve the economy of the process, the resinous product is preferably recovered from the slack wax. As pointed out above, the bulk of the product is precipitated and separated out along with the wax. This product may be conveniently and economically recovered by heating

the slack wax in the presence of a suitable solvent which precipitates the product, such as a ketone or alcohol, at a temperature above the melting point of the wax. As a specific example, the slack wax was heated in boiling methyl ethyl ketone with the result that the product was largely precipitated from the wax solution and a 60% recovery of the product based upon the original quantity of the resinous material employed was obtained. This 60% recovered resin was then used again on the original full quantity of oil to be dewaxed, with the result that as good filtration time, yield of dewaxed oil and other tests were obtained as in the original dewaxing tests with the full 100% quantity of the original product. It therefore appears that the most effective constituents of the resinous material which are effective as dewaxing aids are largely recovered by this treatment. When this recovered product is recycled for additional dewaxing and is separated from the slack wax in a subsequent operation, a substantially higher recovery of this concentrated product than the 60% yield mentioned above is obtained by the method set out above. The net result is that the loss per cycle of active dewaxing aid is reduced to a comparatively small figure thereby effecting substantial economy in the process.

The resinous product of this invention is found to be highly effective in the presence of wet solvent, does not materially change the neutralization and saponification numbers of the dewaxed oil, does not discolor a pale oil, and does not objectionably increase the carbon residue of the dewaxed oil. Any small proportion of the product which remains in solution in the dewaxed oil is found unobjectionable, and may even have a beneficial effect in somewhat improving the viscosity index and other properties of the dewaxed oil.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the dewaxing of wax-bearing mineral lubricating oil by filtration in the presence of a dewaxing solvent containing a small amount of water, the method of substantially increasing the rate of filtration without causing substantial discoloration of the resulting dewaxed oil and without substantially increasing its neutralization and saponification numbers, which comprises incorporating in the oil, in small proportion, prior to filtration, a wax crystal modifying resinous material which is a reaction product of rubber with a compound selected from the group consisting of halides and halogen acids of tin and boron, chilling the oil containing the modifier to precipitate wax and filtering the chilled mixture to remove the precipitated wax therefrom.

2. The method of claim 1 in which the oil to be dewaxed is diluted with a dewaxing solvent, and the said resinous material is added in a proportion of 0.1–1.0% on the weight of the oil charged.

3. The method of claim 1 in which the oil to be dewaxed is diluted with a dewaxing solvent, and in which the said diluted mix containing the resinous material is heated to a temperature substantially in excess of the temperature of complete solution of oil in solvent prior to chilling.

4. The method of claim 1 in which the oil to be dewaxed is diluted with a dewaxing solvent mixture of a wax anti-solvent and an oil solvent, the oil solvent comprising benzol, and in which the resinous material is added to the charge in the form of a benzol solution.

5. The method of claim 1 in which the oil to be dewaxed is diluted with a mixture of methyl ethyl ketone and benzol, and the resinous material is added to the diluted oil mix in the form of a benzol solution in a proportion to provide 0.1–1.0% by weight of resinous material on the weight of the oil charged.

6. The method of claim 1 in which the resinous material is recovered from the slack wax resulting from the wax separating step, and the recovered resinous material is recycled for addition to more oil to be dewaxed.

7. The method of claim 1 in which the resinous material is recovered from the slack wax resulting from the wax separating step by precipitating the material from a boiling solution of the slack wax in a ketone solvent of the character of methyl ethyl ketone.

8. The method of claim 1 in which the oil to be dewaxed is diluted with a solvent mixture of a wax anti-solvent and an oil solvent, and in which the wax is separated from the chilled oil by filtration, and the resinous material is then recovered from the slack wax for reuse in the process.

9. In the solvent dewaxing of wax-bearing mineral lubricating oil, the method which comprises adding to the oil a small proportion of a wax crystal modifying material which is a reaction product of rubber and a compound selected from the group consisting of halides and halogen acids of tin and boron in the presence of a chemical agent capable of depolymerizing the rubber to produce a product of lower molecular weight, chilling the oil containing the modifier to precipitate wax and separating the precipitated wax from the oil.

10. In the solvent dewaxing of wax-bearing mineral lubricating oil, the method which comprises adding to the oil a small proportion of a wax crystal modifying material which is a reaction product of rubber with a halide salt of an amphoteric metal in the presence of a chemical agent capable of depolymerizing the rubber to produce a product of lower molecular weight, chilling the oil containing the modifier to precipitate wax and separating the precipitated wax from the oil.

11. In the solvent dewaxing of wax-bearing mineral lubricating oil, the method which comprises adding to the oil a small proportion of a wax crystal modifying material which is a reaction product of rubber with a halide salt of an amphoteric metal in the presence of an acid capable of depolymerizing the rubber to produce a product of lower molecular weight, chilling the oil containing the modifier to precipitate wax and separating the precipitated wax from the oil.

12. In the solvent dewaxing of wax-bearing mineral lubricating oil, the method which comprises adding to the oil a small proportion of a wax crystal modifying material which is a reaction product of rubber in an aromatic solvent and an amphoteric metal in the presence of an acid capable of depolymerizing the rubber to produce a product of lower molecular weight, chilling the oil containing the modifier to precipitate wax and separating the precipitated wax from the oil.

13. In the solvent dewaxing of mineral oil, the method which comprises adding to the oil a small

proportion of a wax crystal modifying material which is a reaction product of rubber and stannic chloride in the presence of glacial acetic acid, chilling the mixture to precipitate wax and separating the precipitated wax from the oil.

14. In the solvent dewaxing of mineral oil, the method which comprises adding to the oil a small proportion of a wax crystal modifying material which is a reaction product of rubber in an aromatic solvent in the presence of glacial acetic acid and stannic chloride, chilling the mixture to precipitate wax and separating the precipitated wax from the oil.

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