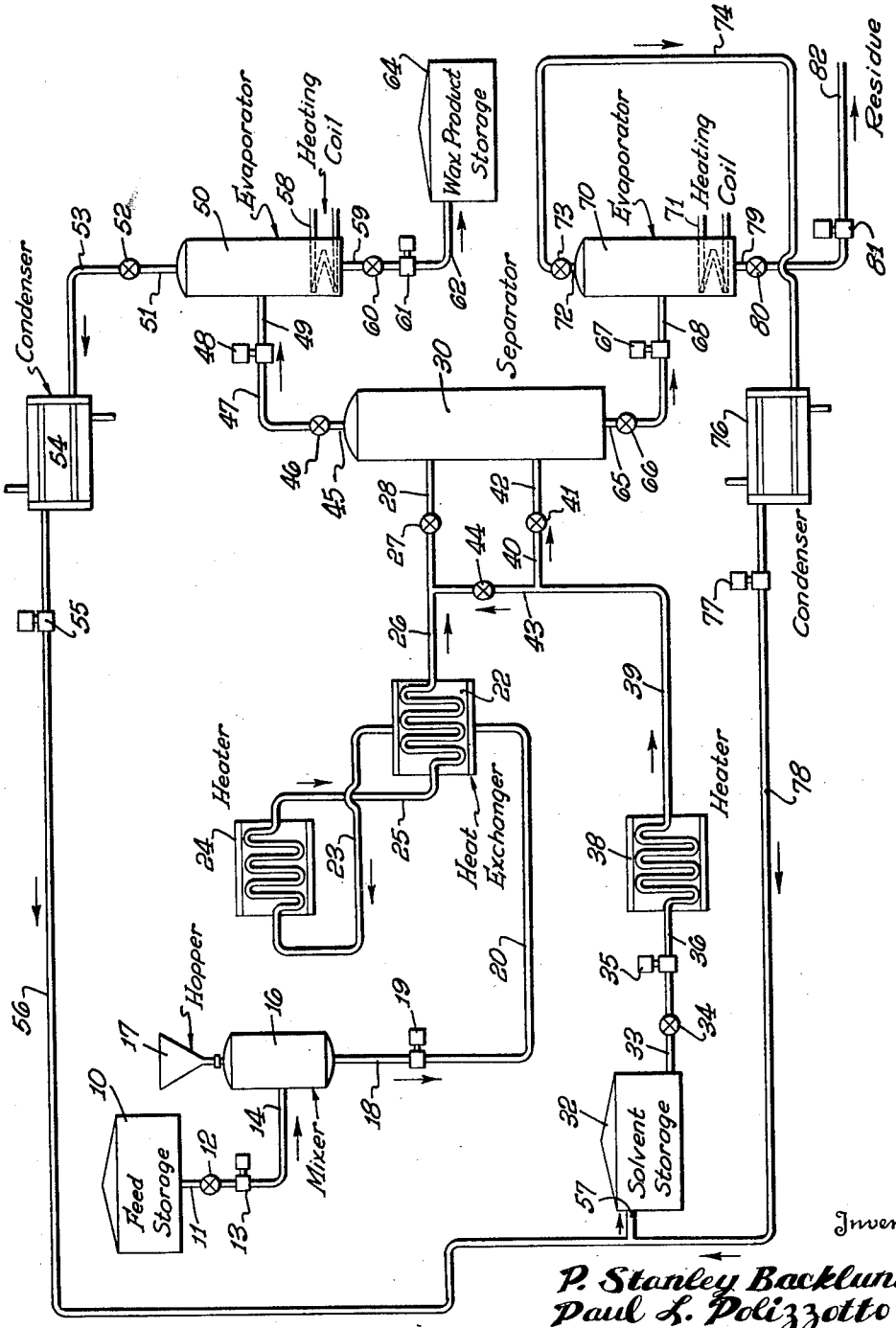
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REFINING OF WAX

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## REFINING OF WAX

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This invention relates to the refining and decolorization of wax by the separation of the dark colored asphaltic and resinous materials therefrom. More particularly this invention relates to the refining of those petroleum waxes which are especially difficult to refine and require excessive amounts of clay, solvent, sulfuric acid or the like to decolorize them satisfactorily.

Petroleum waxes are high molecular weight, naturally occurring hydrocarbons which melt in the temperature range of 100° F. to 200° F. or higher, and are colorless or nearly so when suitably refined. They comprise normal and isoparaffins and possibly naphthenes containing long paraffin chains, which compounds contain approximately 20 to 40 carbon atoms and are found in petroleum distillates particularly lubricating oil fractions in which they are associated with normally liquid hydrocarbons of the same boiling range. The waxes are necessarily separated and removed from these fractions in order to obtain lubricating oils having satisfactory low temperature characteristics. The waxes separated therefrom constitute valuable by-products and when suitably refined are readily marketable.

Petroleum waxes often separate on long standing from paraffin-containing crude oils and these wax deposits are commonly found in the bottom of storage tanks and in transfer lines. Similar waxes are deposited on sucker rods in oil wells. The decolorization of these waxes is difficult because of their high asphalt and resin content which generally exceeds 5 weight per cent. Collectively these materials are referred to in the trade as tank bottoms.

Refined waxes which have been overheated in processing and are consequently discolored are also difficult to decolorize. Certain commercially available activated clays are highly effective for the refining of waxes obtained from petroleum distillates, but are of little value for the decolorization of both overheated wax and tank bottoms wax.

Many processes are currently employed to dewax wax-oil mixtures. In general, these processes involve the principle of chilling the wax-oil mixture in the presence of a diluent or solvent comprising ketones, alcohols, aromatics, chlorinated hydrocarbons, petroleum naphthas or the like such that the wax is precipitated and can then be separated by filtration. The solvent is recovered from both streams by distillation and/or evaporation. Wax contaminated with varying amounts of oil is obtained from these

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processes and is commonly known as "slack wax." The removal of the contaminating oil is accomplished by a deoiling process which involves solution of the slack wax in one of the above solvents and again chilling so as to obtain a substantially oil-free wax. The oil separated in the deoiling step after removal of the solvent is known as foots oil. An older and less efficient process of deoiling which is still widely used in the industry involves the "sweating" of the solidified wax so that the oil slowly separates from the wax, drains, and is removed in pans placed underneath.

Regardless of the method of deoiling the resulting wax is dark colored due to the presence of asphaltic and/or resinous materials. The color of the crude wax may range from light yellow to dark brown, or even black, depending on the source of the wax and on the concentration of the color bodies.

Asphalts are generally believed to be high molecular weight bodies which are carbon-rich and hydrogen-lean and contain oxygen and generally sulfur. These materials presumably contain many highly condensed ring systems and are dark colored. Resins are similarly high molecular weight materials but are probably less highly condensed than asphalts and in addition are more soluble than asphalts in hydrocarbon fractions under certain conditions. In the following description the terms asphaltic and resinous material are taken to be synonymous with color bodies inasmuch as these compounds are believed to be responsible for the color existing in the crude petroleum waxes.

Prevailing market conditions demand the removal of these color bodies for most commercial purposes. The common methods for decolorizing these waxes involve: (1) acid treatment with sulfuric acid, (2) treatment with an adsorbent such as an activated clay, (3) solution in a solvent such as a light hydrocarbon which precipitates the color bodies, or combinations of these processes.

Acid treatment is necessarily conducted at a temperature suitable to maintain the wax in a liquid state during the treating. Such temperatures increase the severity of the acid treating step thereby giving rise to side reactions and also yield sludges which are often difficult to separate from the melted wax. Moreover, a final clay treatment is generally required to finish the acid treated wax. Even after such treatments, some waxes and particularly those referred to as tank bottoms are not completely decolorized.

Many modifications of clay treating are known

and the following procedure is of commercial application. A deoiled wax is heated to a temperature above its melting point, for example, 300° F. and percolated through a column of an adsorbent material such as clay, bauxite, fuller's earth, or the like. With certain types of waxes this method of refining is decidedly uneconomical because of large quantities of adsorbent required for satisfactory decolorization. Moreover, it has been found that clay treatment regardless of the amount of clay employed will not completely decolorize waxes of the types described as tank bottoms or waxes which have been darkened by overheating.

The third type of decolorizing procedure mentioned above usually employs a liquefied normally gaseous hydrocarbon at elevated temperatures, for example, propane at 100° F. to 200° F. thereby precipitating the asphalt from the wax in solvent solution. This latter method permits the decolorizing and deoiling steps to be effected in the presence of the same solvent. For example, the crude wax is dissolved in liquid propane and heated to the desired deasphalting temperature under a pressure sufficient to maintain propane in a liquid state. The wax remains dissolved in the propane-rich phase while the asphaltic bodies are mostly precipitated under these conditions. After removal of the asphalt-rich propane-lean lower phase, the propane-wax-oil mixture can be chilled to the dewaxing temperatures by the evaporation of the required amount of propane under reduced pressure. A deoiled and deasphalted wax is precipitated therefrom and is removed by filtration. The propane solvent is recovered throughout by either evaporation and/or distillation. The principal disadvantage of this process lies in the high pressures necessary to maintain the propane in a liquid state at the deasphalting temperature. Another disadvantage is that complete decolorization is not always effected.

It is therefore an object of this invention to provide a new and economical process for decolorizing petroleum waxes.

It is another object of this invention to refine and decolorize more economically those waxes which have heretofore been difficult and costly to decolorize by known treating procedures.

Further it is an object of this invention to provide an economical and effective process for the decolorization of any wax containing contaminating asphaltic and/or resinous color bodies.

Still another object of this invention lies in the decolorization and deoiling of wax-oil-asphalt-resin mixtures in a continuous and economical process.

It is a particular object of this invention to provide a process for the decolorization of waxes involving the use of activated magnesium oxide in conjunction with a solvent.

Other objects and advantages of the invention herein disclosed will become apparent to those skilled in the art as the description thereof proceeds.

The process of this invention involves treating a wax containing asphaltic and/or resinous material at a temperature of at least about 275° F. and preferably between 300° F. and 400° F. with 5% to 25% and preferably 10% to 20% by weight of magnesia. The treatment consists in thoroughly mixing and contacting the wax with the magnesia for a period of 5 to about 45 minutes, generally a treating time of about 15 to 30 minutes is employed. The resulting mixture is cooled to a temperature of about 150° F. to 275° F. and preferably to a temperature of from 200° F. to 240° F. and at this temperature is extracted with between 2 volumes and about 10 volumes and preferably with between 5 volumes and 7 volumes, based on the wax, of a solvent having a preferential solvency for wax to separate decolorized wax from the magnesia and adsorbed and/or rejected asphaltic and/or resinous materials. After thoroughly mixing and contacting the wax-magnesia mixture with solvent the resulting mixture is permitted to separate into two layers, the upper layer consisting of a solvent solution of wax and the lower layer consisting of magnesia, asphaltic and resinous materials and small amounts of solvent. The layers are separately withdrawn from the separating unit and are separately evaporated to recover solvent, decolorized wax and magnesia together with the asphaltic and resinous materials.

Desirable solvents for use in the process are those which have good solvency for wax and low solvency for asphaltic and resinous materials so that they dissolve the wax and reject the color bodies from solution. These include the lower molecular weight alcohols, ketones and ethers and preferably those alcohols, ketones and ethers which contain less than 6 carbon atoms in their molecular structure. Preferably the alcohol, ketone or ether will be one having 3 to 5 carbon atoms in the molecule although in certain instances ethyl alcohol may be employed particularly if used in conjunction with a 4 or 5 carbon atom alcohol, ketone or ether. Thus solvents which may be employed include ethyl alcohol, propyl alcohol, isopropyl alcohol, normal, iso and tertiary butyl alcohols and the normal, iso and tertiary amyl alcohols; acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone and methyl isopropyl ketone; methyl ethyl ether, diethyl ether, methyl propyl ether, methyl isopropyl ether, ethyl propyl ether and the like. The mentioned alcohols, ketones and ethers are all saturated, aliphatic compounds containing less than 6 carbon atoms per molecule. In addition to the individual compounds indicated herein, various mixtures of two or more of these compounds may be employed as solvents. In some instances it appears to be desirable to employ a solvent consisting of a 3 carbon atom alcohol, ketone or ether with a 4 or 5 carbon atom alcohol, ketone or ether. By varying the proportion of the lower and higher carbon atom compounds in the solvent it is possible to obtain a solvent having the most desirable solvency for wax at any given temperature of extraction.

The particularly preferred solvents of the above group are those containing 3 carbon atoms per molecule and of these isopropyl alcohol, acetone and methyl ethyl ether appear to have the most desirable solvency characteristics. However, as indicated above, it is sometimes desirable, depending upon the temperature to be employed in the extraction step, to employ alcohols, ketones or ethers of 4 or 5 carbon atoms together with the isopropyl alcohol, acetone or methyl ethyl ether in order to improve the solvency for wax of these solvents.

The particular kind of magnesia employed in our process is of importance inasmuch as it has been found that while all magnesias appear to be operable they are not equally suitable for use in the disclosed process. Generally speaking, any magnesia possessing a high specific surface and/or high adsorbability is a suitable adsorbent

and in the description such magnesias will be referred to as activated magnesias.

An inexpensive activated magnesia suitable for the process disclosed herein was prepared from the mineral dolomite

(approximately $MgCO_3 \cdot CaCO_3$)

by heating the ore to 2000° F. to convert it to the double oxide, treatment with decarbonated water to form the double hydroxide, washing the double hydroxide with decarbonated water to leach out the more soluble calcium hydroxide, drying the resulting magnesium hydroxide, and calcining the hydroxide to form the activated magnesia. The drying of the magnesium hydroxide may be carried out in an oven or kiln at about 250° F. The calcination of the magnesium hydroxide to form the activated magnesia may be carried out in the same apparatus but is preferably carried out in a second kiln or furnace at a temperature in the range of 300–900 or 1000° F. and preferably in the range of 400–700° F. The product is preferably ground to finer than 325 mesh prior to use for wax decolorization although if ground until 90% passes through a 250 mesh screen it is satisfactory.

The following chemical analysis was obtained on a sample of magnesia prepared by the above method and dehydrated by heating to 700° F.

| Constituent: | Percentage by weight |
|---|---|
| MgO | 87.81 |
| CaO | 1.68 |
| $SiO_2$ | 0.49 |
| NaCl | 0.25 |
| $SO_3$ | 0.87 |
| Loss on ignition (800° C.) | 8.91 |
| Total | 100.00 |

Obviously magnesias may be prepared by other processes such as precipitation of magnesium hydroxide from soluble magnesium salts followed by dehydration and conversion of the hydroxide to the oxide. Such magnesias produce the desired color improvement in waxes when employed in our magnesia-solvent process.

Magnesias of the type indicated which are found to have exceptional decolorizing ability when applied to waxes containing asphaltic and/or resinous materials and extracted with solvent are found to be very inefficient decolorizing agents for treatment of lubricating oil fractions and the like. Apparently these magnesias have a specific action in removing color bodies from waxes of the type indicated when the treatment is carried out in conjunction with solvent extraction as described herein.

Our invention may be more readily understood by reference to the drawing. In the drawing the colored or asphalt-containing wax is taken from tank 10, wherein it is maintained as a liquid by steam coils or the like, via line 11 controlled by valve 12 pumped by pump 13 through line 14 into the mixing chamber 16. Activated magnesia is removed from hopper 17 and passed into mixer 16 wherein the magnesia and wax are intimately mixed. The mixture is withdrawn from the mixing chamber 16 via line 18 pumped by pump 19 through line 20 into a heat exchanger 22, wherein it is exchanged with the heat treated mixture and is passed from heat exchanger 22 through line 23 into heater 24 wherein it is heated to the magnesia treating temperature of about 300° F. or above, passing therefrom through line 25 back to heat exchanger 22 wherein it is interchanged with fresh feed as above described to reduce the temperature to the desired extraction temperature as for example about 200° F. to about 230° F. The wax-asphalt magnesia mixture is discharged from heat exchanger 22 through line 26 controlled by valves 27 and 44 through line 28 into the separator or extraction column 30.

The solvent which may be an alcohol, ketone or ether having from 3 to 5 carbon atoms in its molecular structure or any mixture of such alcohols, ketones and ethers is taken from the solvent storage tank 32 through line 33 controlled by valve 34 and pumped by pump 35 through line 36 into heater 38 wherein the solvent is heated to a temperature corresponding to that of the feed leaving the heat exchanger 22, passing from heater 38 through line 39 into lines 40 or 43 controlled by valve 41 or 44 respectively. If it is desired to employ countercurrent extraction the feed is introduced to the extractor through line 28 as described above and the solvent passes from line 40 controlled by valve 41 through line 42 at a point below line 28. If, however, it is desired to employ concurrent extraction valve 41 remains closed and valve 44 is open and the solvent passes through line 43 and is mixed with the feed in line 26, the mixture passing therefrom through valve 27 and line 28 into the separator 30. In the separator the asphalt and magnesia settle to the bottom being continuously withdrawn therefrom through line 65 controlled by valve 66 and pumped by pump 67 through line 68 into evaporator 70. Evaporator 70 is equipped with a heating coil 71 whereby the temperature of the asphalt may be maintained at the temperature of extraction or may be increased if necessary to cause the solvent to vaporize therefrom passing overhead from evaporator 70 through line 72 controlled by valve 73 through line 74 into condenser 76 from which it is pumped by pump 77 through lines 78 and 57 back to solvent storage tank 32. The solvent-free asphaltic residue is withdrawn from evaporator 70 via line 79 controlled by valve 80, is pumped by pump 81 through line 82 to discard or storage as desired.

The upper phase in separator 30 comprising the wax-solvent solution from which the asphaltic and resinous materials as well as the added magnesia has separated is withdrawn via line 45 controlled by valve 46 via line 47 and is pumped by pump 48 through line 49 into evaporator 50 equipped with heating coil 58 wherein the solvent is evaporated from the wax. The vaporized solvent passes overhead through line 51 controlled by valve 52 via line 53 into condenser 54 and the condensed solvent is pumped therefrom by pump 55 through lines 56 and 57 back to the solvent storage tank 32. The solvent-free wax is withdrawn from evaporator 50 via line 59 controlled by valve 60 and is passed by means of pump 61 through line 62 into the wax product storage tank 64. Many modifications of this process may occur to those skilled in the art without departing from the spirit and scope of our invention. Thus an additional clay or other adsorbent treatment or acid treatment may be used before or after the combination magnesia-solvent extraction treatment.

Other modifications of the decolorization process include the treatment of a wax-oil-asphalt mixture in such a manner that the deasphalting and deoiling of the wax are accomplished consecutively with the use of only a single solvent. Thus, a slack wax may be processed in the above described manner with the result that an oil-

solvent-wax solution is obtained in the upper phase of the separator 30 whereafter it is chilled to a temperature sufficiently low to precipitate the wax therefrom. The oil remains in solution and is separated from the solvent by evaporation; the solvent is recycled and the oil is sent to storage. The deoiled and decolorized wax is removed from the chilled oil-solvent mixture by filtration. The solvent adhering to or occluded by the precipitated wax is recovered by evaporation. It is apparent, therefore, that by our process we are able to treat either a wax-asphalt mixture or a wax-oil-asphalt mixture by a variety of procedural methods to obtain oil-free wax of considerably reduced asphalt content and having a correspondingly lighter color.

The following example will serve to illustrate further the invention.

A black tank bottoms wax melting at 196° F. and containing about 5% by weight of asphaltic and resinous materials, which was jet black in color and was obtained from a California waxy crude oil storage tank, was heated to 310° F. in the presence of 15 weight per cent of an activated magnesia containing 8.9 weight per cent volatile matter and of the type prepared from dolomite. The mixture was immediately cooled to a temperature of 210° F. and agitated for 15 minutes in the presence of 6 volumes of isopropyl alcohol, whereafter it was allowed to settle for 45 minutes. The upper phase was separated and the solvent removed by distillation, whereupon a light tan wax having an American melting point of 190° F. was obtained.

The foregoing description of our invention for decolorizing impure waxes is specific and is meant only to be illustrative of our invention which comprises the extraction of any wax-asphalt or wax-asphalt-oil mixture in the presence of an activated magnesia with solvents comprising alcohols, ketones, and ethers of from 3 to 5 carbon atoms or mixtures thereof, and preferably the alcohols, ketones, and ethers of 3 carbon atoms or mixtures thereof to separate selectively a decolorized wax from the asphaltic and resinous contaminants.

Having fully described our invention and the advantages accruing therefrom and appreciating the fact that many modifications thereof may occur to those skilled in the art without departing from the spirit or scope of the invention, we claim:

1. A process of decolorizing wax containing asphaltic and resinous color bodies which comprises contacting said wax with magnesia at a temperature above the melting point of the wax, extracting the resulting mixture of wax and magnesia with a solvent comprising a compound selected from the class consisting of the saturated aliphatic alcohols, ketones and ethers containing less than 6 carbon atoms per molecule, and separating a solvent solution of decolorized wax from a mixture of magnesia and said color bodies.

2. A process according to claim 1 wherein the solvent consists of a mixture of isopropyl alcohol and methyl ethyl ketone.



3. A process of decolorizing wax-containing asphaltic and resinous color bodies which comprises contacting said wax with magnesia at a temperature between 275° F. and 400° F., extracting the resulting mixture of wax and magnesia with a solvent selected from the class consisting of the saturated aliphatic alcohols, ketones, and ethers containing less than 6 carbon atoms per molecule, and separating a solvent solution of decolorized wax from a mixture of magnesia and said color bodies.

4. A process according to claim 3 wherein the solvent is acetone.

5. A process according to claim 3 wherein the solvent is isopropyl alcohol.

6. A process according to claim 3 wherein the solvent is methyl ethyl ether.

7. A process for decolorizing tank bottoms wax-containing at least about 5 weight per cent of asphaltic and resinous materials which comprises contacting said wax with 10 to 20 weight per cent of activated magnesia at a temperature between about 275° F. and 400° F., extracting the resulting mixture with between about 2 volumes and about 10 volumes, based on the wax, of a solvent selected from the class consisting of the saturated aliphatic alcohols, ketones, and ethers containing 3 to 5 carbon atoms per molecule, and separating a solvent solution of decolorized wax from a magnesia-asphalt-resin mixture.

8. A process according to claim 7 wherein the magnesia is prepared by calcining the mineral dolomite at about 2000° F. to form a mixture of calcium oxide and magnesium oxide, converting the oxides into the corresponding hydroxides, washing the product with water to leach out the calcium hydroxide, drying the resulting magnesium hydroxide, and finally calcining the magnesium hydroxide at a temperature below about 900° F.

9. A process according to claim 7 wherein the magnesia is prepared by precipitating magnesium hydroxide by the addition of an alkali metal hydroxide to a water soluble magnesium salt, washing the precipitate to remove impurities, drying, and finally calcining at a temperature below 900° F.

10. A process according to claim 1 wherein the solvent consists of a mixture of a saturated aliphatic alcohol and a saturated aliphatic ketone each containing less than 6 carbon atoms per molecule.

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