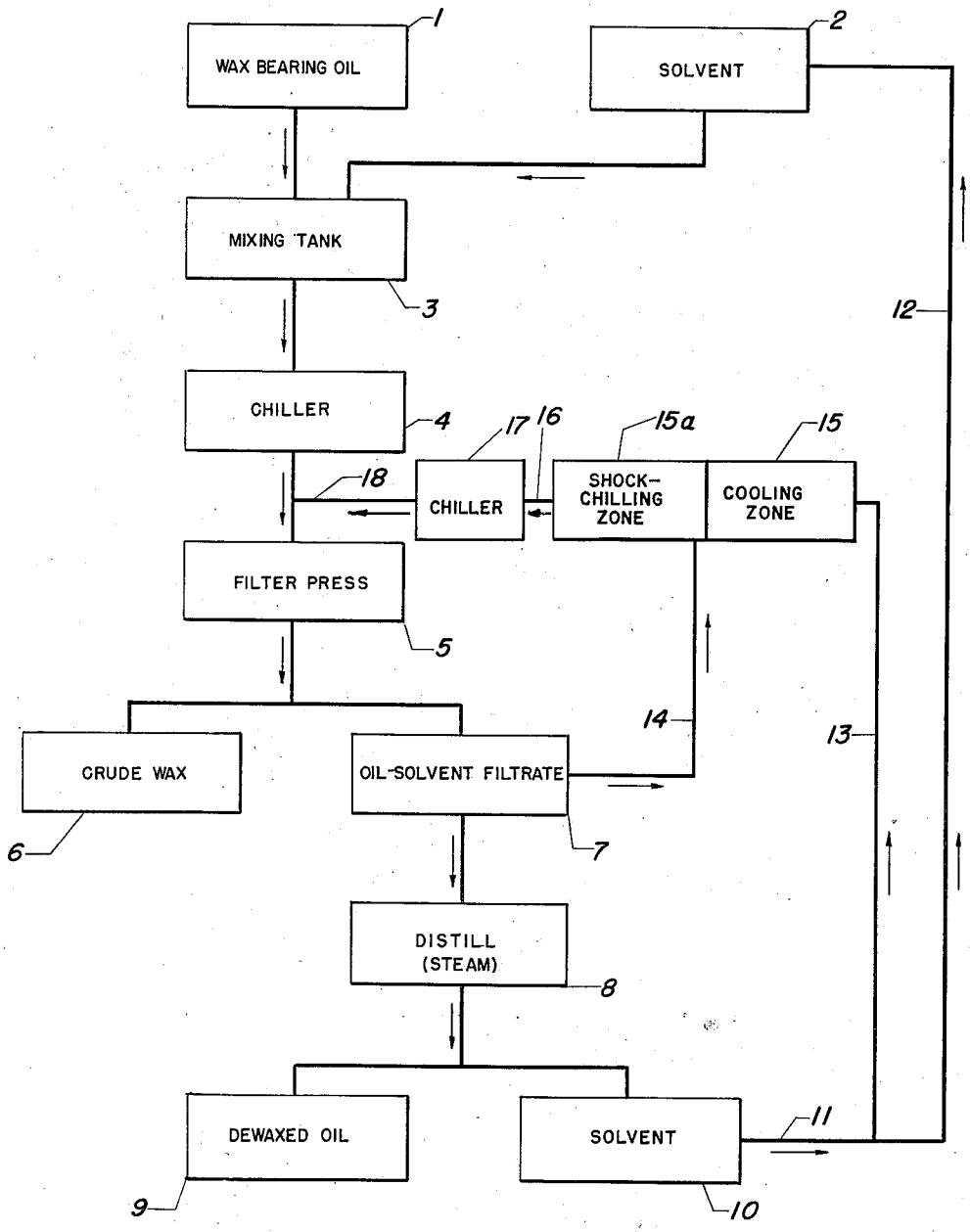
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CHILLING OF OILS

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CHILLING OF OILS

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This invention relates to an improvement in the solvent dewaxing of petroleum lubricating oil fractions.

Petroleum fractions of the nature of distillates and residues and mixtures thereof containing waxy materials are normally treated to remove the wax therefrom by adding to the waxy oil a diluent material, chilling the mixture to a temperature at which the wax or a substantial portion thereof is precipitated and thereafter filtering, centrifuging, or otherwise physically separating the wax from the oil. Those methods in which the diluent used is one tending to exert a prefential solvent action for oil over waxy material at low temperatures are commonly known as solvent dewaxing methods.

In carrying out solvent dewaxing treatment of waxy oil stocks, it has heretofore been one of the conventional practices to dilute the stock initially with only a portion of the solvent ultimately present in the filtration stage, to chill the resulting mixture, precipitating a substantial portion of the wax, and thereafter to add a secondary portion of pre-chilled solvent to the mix, chilling the whole to separation temperature and separating the wax therefrom. The above practice has proved advantageous in affording an increased ability to control the physical nature of the filter cake and in generally providing an improved yield of dewaxed oil from a given stock.

The chilling of the initial oil-solvent blend and of the secondary portion of solvent in the above operation is ordinarily accomplished by passing the material to be chilled through suitable refrigeration equipment, representative of which is a double pipe chiller of the Carbondale type. This machine consists of a number of pipes in series, each jacketed by an outer pipe of larger diameter. A cooling medium, such as brine solution or the like, is circulated between the two pipes, thus chilling the surface of the inner pipe through which the oil-solvent mixture or solvent is passed. Inside of each of the pipes is a screw-like scraper composed of a central shaft with a helical scraper blade attached thereto. The scraper is revolved during the chilling operation, the blade thereof touching the inner surface of the pipe, removing any adhering solid matter therefrom and forcing the same along and out of the pipe.

It has heretofore been noted in dewaxing petroleum stocks in accordance with the above procedure that when the secondary portion of solvent is refrigerated, in the absence of oil, prior to addition to the mix, a small quantity of water

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dissolved in the solvent is deposited as a hard, adherent ice formation on the heat transfer surfaces of the chilling equipment. This layer of ice greatly interferes with the efficiency of the chiller and acts as a partial insulator, tending to inhibit further cooling of the solvent. Where, as is usually the case, a chiller of the Carbondale type is employed, the formation of a hard ice coating on the cooled surface of the inner pipe of the chiller leads to plugging of said chiller and, ultimately, in causing breakage of the blades of the revolving scraper.

This problem of ice formation in the chilling equipment is particularly prevalent when the dewaxing solvent or solvent mixture employed has a tendency to dissolve water. In practice, it is necessary to recover the solvents employed for further use in treating fresh oil-wax mixtures. A customary method of recovering solvent from the dewaxed oil is by steam distillation of the oil-solvent mixture, which tends to leave a certain amount of water incorporated in the solvent. Further use of such recovered solvents leads to the deposition of hard ice crystals in the chilling operation, giving rise to the aforesaid difficulties.

One method of overcoming the problem is to remove water from the solvent employed. This method, however, has not been practiced to any great extent, due primarily to the expense of the operation involved. In some instances, a drying agent has been used, such as concentrated sodium carbonate solution, for drying the solvents prior to use or recovered from the oil and wax fractions by distillation. In practice, this procedure has consisted of contacting the solvent containing a small quantity of water with the solution of drying agent until the drying agent is so diluted that no further water is absorbed from the solvent. A portion of the diluted solution is then discarded and fresh concentrated solution is added to the remainder to maintain the absorption capacity of the drying agent at the proper level. In discarding a portion of the diluted solution, not only is some of the drying agent lost, but an appreciable quantity of the solvent is lost, since such diluted solution is saturated with solvent at the treating temperature.

It is an object of the present invention to overcome the aforementioned difficulties present in the chilling operation of solvent dewaxing by preventing the formation of a hard, adherent ice on the walls of the chiller employed in refrigerating the solvent. A more specific object is to prevent the breakage of chiller scraper blades, due to contact with said hard ice forming on the

surfaces of the inner pipe of double pipe chillers conventionally employed in the art. A further object is to prevent the plugging of chiller pipes. A still further object is to inhibit the formation of an ice coating on the chiller pipes, which interferes with the chilling effect of the surrounding cooling medium, acting as a partial insulator against the same.

These and other objects which will be recognized by those skilled in the art are realized in accordance with the present invention. It has now been found that the adherence of ice on the inner surfaces of the chilling equipment can be substantially inhibited by cooling the solvent containing aqueous contaminant to just above the temperature at which the formation of ice crystals takes place and thereafter shock-chilling the wet solvent with a cold stream of oil which preferably has been previously freed of wax. The ice crystals so obtained as a result of shock-chilling are suspended in the resulting oil-solvent mixture and may either be removed therefrom by filtration or retained in the oil-solvent mixture while the same is further processed. In the latter instance the suspension of ice crystals in the oil-solvent mixture readily moves through the chiller pipes to the initial waxy oil-solvent mixture and is subsequently removed therefrom upon filtration along with the wax cake from which it is easily separated by simply allowing the ice crystals to melt.

While the scope of the present invention is, of course, not to be unduly limited by any theory, it would appear that in shock-chilling the wet solvent with pre-chilled oil, the oil acts as a lubricant between the ice crystals so formed and the surfaces of the chilling equipment, thereby preventing the ice crystals from adhering to the walls of the chiller. On the other hand, if the wet solvent is shock-chilled in the absence of oil, the ice crystals formed separate on the walls of the chiller, giving rise to the aforementioned operational difficulties.

A particularly preferred embodiment of the present invention is the shock-chilling of the wet solvent by a cooled stream of dewaxed oil-solvent mixture, resulting as filtrate upon separation of the wax from the initial solvent dewaxing of the stock undergoing treatment. This procedure may be more readily understood by reference to the simplified flow diagram attached hereto. Referring more particularly to said diagram, a wax-bearing oil 1 and a dewaxing solvent 2, corresponding in amount to between about 0.5 and about 7.0 volumes of the total volume of oil being treated, are mixed in tank 3. After thorough agitation of oil and solvent, the resulting mixture is conducted to chiller 4 and cooled to a dewaxing temperature of between about −25° F. and about 20° F. The wax precipitated upon cooling is removed by passing the oil-solvent wax slurry through a press 5, leading to separation of crude wax 6 and an oil-solvent filtrate 7. The filtrate is then steam-distilled in fractionation apparatus 8 to effect a separation into dewaxed oil 9 and solvent 10. The solvent is recycled through conduits 11 and 12 to supplement the initial solvent supply at 2. It has heretofore been conventional to withdraw a side stream of the recovered solvent and to recycle the same with chilling in the absence of oil. It is this chilling step which has resulted in the aforementioned difficulties of ice formation, due to aqueous contaminant present in the solvent being cooled. In accordance with the present procedure, such ice adherence on the

walls of the chilling equipment is eliminated by cooling the solvent in cooling zone 15 to a temperature just above that at which the formation of ice crystals takes place, and thereafter shock-chilling with an injected stream of cold oil-solvent filtrate 7 passing through conduit 14 to shock-chilling zone 15a. The resulting shock-chilled oil-solvent mixture contains ice crystals suspended therein. This suspension of ice passes readily through the shock-chilling zone and through conduit 16 and then through chiller 17 and conduit 18 where it joins the initial waxy oil-solvent mixture prior to filter-pressing. The ice crystals present are readily removed along with the wax cake by filtration and are thereafter separated from the crude wax by simply allowing the ice to melt.

Upon operation in accordance with the above procedure, the difficulties heretofore encountered involving plugging of the chiller pipes, due to hard, adherent ice formation therein with resultant chipping and breaking of the chiller scrapers, has thus been overcome.

The process of this invention has been found to be particularly useful in procedures employing solvent mixtures which have a relatively high tendency to dissolve water, such as those containing ketones. Hence, the process described herein has been found to be suitable for processes using ketone-benzol dewaxing solvents, such as mixtures containing 35 to 55 per cent acetone or methyl ethyl ketone, 5 to 35 per cent toluol, and 10 to 60 per cent benzol. The aqueous contaminant present in said solvent mixtures is generally between about 0.4 and about 1 per cent by weight.

The particular ratio of solvents to be used will be largely dependent on the characteristics of the oil under treatment. In general, a larger proportion of benzol or toluol necessitates the use of lower chilling temperatures to obtain an oil of a given pour test. In practice, the oil to be dewaxed is diluted with a portion of the solvent ultimately present in the filtration stage. This initial amount of solvent will usually correspond to between about 0.5 and about 3.0 volumes per unit volume of oil being treated. The initial quantity of solvent added is generally such as to maintain the wax-bearing mass in a liquid state during the chilling and dewaxing operation. The secondary portion of solvent will generally be between about 2.0 and about 3.0 volumes per unit volume of oil initially present. The volume ratio of initial to secondary quantities of solvent employed will thus generally be between about 0.25 to 1 and about 1 to 1.

The secondary quantity of solvent added is generally cooled to a temperature less than 10° F. and preferably less than 5° F. above that at which the formation of ice crystals takes place. Under usual operating conditions, the solvent will be chilled to a temperature between about 35° F. and about 40° F. and then shock-chilled with injected oil to a temperature between about 25° F. and about 5° F. The shock-chilled mixture may thereafter be further cooled to 0° F. or lower temperatures if desired.

The amount of pre-chilled oil or oil-solvent mixture used in shock-chilling the cooled secondary quantity of solvent is an amount sufficient to lower the temperature of the solvent at a rapid rate below the freezing point of water and hence to yield a suspension of ice crystals contained in the resulting oil-solvent mixture. The particular quantity of pre-chilled oil used will be

dependent on the amount of solvent to be chilled, on the temperature of said solvent and on the temperature of the injected oil. Where the injected pre-chilled oil constitutes the oil-solvent filtrate resulting from an initial pressing of the wax cake, the volume ratio of the side stream of cold oil-solvent filtrate being led to the chiller employed for cooling the secondary quantity of solvent to the main stream being conducted to distillation will generally be between about 0.25 and about 1.0.

Having described the nature of this invention, a following typical example of operation in accordance therewith is set forth below:

Example

One volume of waxy oil having a Saybolt Universal viscosity of 75 seconds at 30° F., and containing 12 per cent wax, was mixed with one volume of dewaxing solvent consisting of 40.2 per cent methyl ethyl ketone, 40 per cent benzene, 19.2 per cent toluene, and 0.6 per cent water. The resulting mixture was chilled to a temperature of 0° F. One and one-half volumes, based on the oil charge, of additional solvent having the above composition were chilled to 35° F. and thereafter mixed with 1½ volumes of recycled filtrate emerging from the filters as shown in the attached diagram at a temperature of 0° F. The recycled filtrate contained about 75 per cent solvent and about 25 per cent dewaxed oil. The resulting mixture of the secondary quantity of solvent and filtrate was then chilled to 0° F. and mixed with the primary solvent-waxy oil mixture. By employing the above procedure of shock-chilling the secondary quantity of solvent with recycled filtrate, the adherence of hard ice crystals on the heat transfer surfaces of the filters was substantially inhibited.

Thus, the above procedure clearly shows that through the steps of cooling a solvent mixture containing aqueous contaminant to just above that at which the formation of ice is encountered and thereafter shock-chilling the cooled solvent with pre-chilled oil, a suspension of ice crystals in the resulting oil-solvent mixture is obtained, which thereby eliminates the formation of an adherent ice cake on the inner walls of the heat transfer surfaces of the chilling equipment. The expensive and troublesome breakage of chiller scrapers is prevented and the pre-treatment of solvents with drying agents to remove water therefrom, as has heretofore been necessary, is thus eliminated to provide an improved flow rate of the liquid solvent mixture through the chiller tubes and hence to afford an overall, more efficient dewaxing process.

I claim:

1. A method of dewaxing a wax-bearing oil, comprising the steps of: blending said oil with a dewaxing solvent containing a minor proportion of aqueous contaminant, chilling the resultant mixture to precipitate wax therefrom, cooling a separate secondary portion of said solvent to a temperature just above that at which the formation of ice takes place therein, conducting said cooled secondary portion of solvent to a shock-chilling zone maintained at a temperature below the freezing point of water with an injected oily chilling agent prepared as hereinafter described, cooling the shock-chilled secondary portion of solvent to a temperature approximately equal to that of the primary chilled solvent mixture of wax and oil, adding the cooled shock-chilled secondary portion of solvent to the primary chilled solvent mixture of wax and oil, the temperatures of the two solvent mixtures being approximately identical at this point, filtering wax from the resulting composite mixture, yielding an oil-solvent filtrate, recycling said filtrate for use as the aforesaid oily chilling agent to yield, as a result of the initial cooling and subsequent shock-chilling of said secondary portion of solvent, a suspension of ice crystals in the oil-solvent mixture so obtained, thereby inhibiting the formation of a hard, adherent ice in the aforesaid shock-chilling zone.

2. A method of dewaxing a wax-bearing oil, comprising the steps of: blending said oil with a dewaxing solvent containing a minor proportion of aqueous contaminant, chilling the resultant mixture to precipitate wax therefrom, cooling a separate secondary portion of said solvent to a temperature less than 5° F. above the temperature at which the formation of ice takes place therein, conducting said cooled secondary portion of solvent to a shock-chilling zone maintained at a temperature below the freezing point of water with an injected oily chilling agent prepared as hereinafter described, cooling the shock-chilled secondary portion of solvent to a temperature approximately equal to that of the primary chilled solvent mixture of wax and oil, adding the cooled shock-chilled secondary portion of solvent to the primary chilled solvent mixture of wax and oil, the temperatures of the two solvent mixtures being approximately identical at this point, filtering wax from the resulting composite mixture, yielding an oil-solvent filtrate, recycling said filtrate for use as the aforesaid oily chilling agent to yield, as a result of the initial cooling and subsequent shock-chilling of said secondary portion of solvent, a suspension of ice crystals in the oil-solvent mixture so obtained, thereby inhibiting the formation of a hard, adherent ice in the aforesaid shock-chilling zone.

3. A method of dewaxing a wax-bearing oil, comprising the steps of: blending said oil with a dewaxing solvent containing a minor proportion of aqueous contaminant, chilling the resultant mixture to precipitate wax therefrom, cooling a separate secondary portion of said solvent to a temperature just above that at which the formation of ice takes place therein, conducting said cooled secondary portion of solvent to a shock-chilling zone maintained at a temperature below the freezing point of water with an injected cold stream of oil, adding the shock-chilled secondary portion of solvent to the primary chilled solvent mixture of wax and oil, the temperatures of the two solvent mixtures being approximately identical at this point, filtering the resulting mixture to separate wax therefrom, yielding, as a result of the initial cooling and subsequent shock-chilling of said secondary portion of solvent, a suspension of ice crystals in the oil-solvent mixture so obtained, thereby inhibiting the formation of a hard, adherent ice in the aforesaid shock-chilling zone.

4. A method of dewaxing a wax-bearing oil, comprising the steps of: blending said oil with a dewaxing solvent containing a minor proportion of aqueous contaminant, chilling the resultant mixture to precipitate wax therefrom, cooling a separate secondary portion of said solvent to a temperature less than 5° F. above the temperature at which the formation of ice takes place therein, conducting said cooled secondary por-

tion of solvent to a shock-chilling zone maintained at a temperature below the freezing point of water with an injected cold stream of oil, adding the shock-chilled secondary portion of solvent to the primary chilled solvent mixture of wax and oil, the temperatures of the two solvent mixtures being approximately identical at this point, filtering the resulting mixture to separate wax therefrom, yielding, as a result of the initial cooling and subsequent shock-chilling of said secondary portion of solvent, a suspension of ice crystals in the oil-solvent mixture so obtained, thereby inhibiting the formation of a hard, adherent ice in the aforesaid shock-chilling zone.

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