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TROUGH GREASES AND PROCESS OF PREPARING THE SAME

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This invention relates specifically to improved trough grease compositions but more broadly it pertains to improved compositions consisting essentially of microcrystalline hydrocarbon wax and oil with improved luster, smoothness and anti-syneresis properties.

Trough greases are compositions consisting essentially of white oil and microcrystalline wax used extensively for the greasing of pans in commercial baking operations. Since such greases come in contact with and may be partially absorbed by food, it is important that both components be of high purity. The white oil and wax should meet U. S. Pharmacopoeia requirements and the mixture should be free from adulterants. In addition, trough greases must meet strict specifications with respect to smoothness and resistance to syneresis or bleeding. Trough greases may be considered as a special type of petrolatum characterized by higher oil content than ordinary petrolatum and our invention must thus be considered as an improvement in petrolatum compositions. In addition to the high chemical purity required of trough greases, they should be characterized by a pleasing gloss or luster, they should be smooth and not grainy, they should be tasteless and odorless even after prolonged storage, they should meet the necessary requirements of boiling range, viscosity, softness, penetration, melting point, etc. and finally they should be resistant to syneresis, i. e. they should not bleed or permit any oil separation even after prolonged storage at temperatures of the order of 90° F. An object of our invention is to provide an improved trough grease composition which will meet all of the above requirements. A further object is to provide a method and means for improving petrolatums and trough greases produced from Pennsylvania crudes and to produce from mixed base crudes (i. e. Mid-Continent, Texas, coastal, etc.) petrolatums and/or trough greases which will be equal or superior to the best compositions producible from Pennsylvania crudes. Other objects will be apparent as the detailed description of the invention proceeds.

We have discovered that certain low melting point microcrystalline waxes have remarkable and hitherto unsuspected properties of enhancing the tenacity with which higher melting point microcrystalline waxes hold oils with which they are associated. These low melting point microcrystalline waxes are those which have a melting point of approximately 105° F., i. e. within the relatively narrow range of about 95° F. to 115° F.

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Our low melting microcrystalline waxes are characterized by a boiling range within the limits of about 900 to 1150° F. on the true boiling point basis; this sharply distinguishes them from low melting paraffin waxes which boil in the range of about 600 to about 850° F. and even from the so-called motor oil waxes which are somewhat higher boiling than paraffin waxes. Paraffin wax crystals are plate-like in structure and are composed chiefly of straight chain or slightly branched chain hydrocarbon molecules, motor oil wax crystals are in the form of large needles and are composed of paraffinic hydrocarbon molecules which are larger and more highly branched, while microcrystalline waxes have a minute needle structure and are composed chiefly of highly branched hydrocarbon molecules containing about 35 to 55 carbon atoms per molecule.

Microcrystalline waxes when entirely freed from oil have heretofore consisted essentially of high melting wax components, i. e. components having melting points above 120° F. and chiefly in the range of 140° to 165° F. By a recently developed fractionation technique, we have discovered that fractions of crude petroleums having true boiling points in the vicinity of about 1000° F. contain low melting point microcrystalline waxes which have properties differing materially from those of high melting microcrystalline waxes and which apparently contain some ring structure in addition to the highly branched paraffinic hydrocarbon structure. We have discovered that when such low melting microcrystalline waxes are added to ordinary petrolatums in amounts in the range of about 10% by weight, i. e. in the range of approximately 2 to 25% or more, the resulting petrolatum is markedly enhanced in gloss and luster, it is much smoother and less grainy than the original petrolatum and it is substantially free from any tendency toward syneresis or bleeding. Thus, by adding the defined amount of the defined low melting point microcrystalline wax to trough grease formulations, we obtain a product which is vastly superior to previous trough greases.

In the manufacture of petrolatum from Mid-Continent crude petroleum, the crude is distilled to remove components boiling up to and including motor oil distillate (i. e. components boiling up to approximately 1000° F.) and the undistilled portion which is called reduced crude is subjected to conventional deasphalting and/or deresining steps to remove asphalts and resins and give a so-called "steam refined lube stock." This

steam refined lube stock is then acid treated and dewaxed to obtain so-called bright stock and crude petrolatum base, respectively. A crude petrolatum base contains exessive amounts of oil and color bodies and it is, therefore, refined by deoiling procedures, an example of which is multiple washing, recrystallization or reslurrying of solidified wax with light hydrocarbon oil solvents. The washed microcrystalline wax is then percolated through clay for color improvement and a small amount of a refined oil, such as white oil, is added to the final microcrystalline wax to give an ultimate petrolatum product. Ordinary petrolatums may contain about 50 to 80% of oil, but trough greases require a white microcrystalline wax and the use of a still larger amount of white oil in the final composition. Thus, a trough grease usually contains about 85 to 90% of total white oil and only 10 to 15% of oil-free wax; this larger amount of oil presents an extremely vexatious problem because it usually exceeds the amount of oil which the wax can hold and, therefore, leads to syneresis or bleeding.

By careful analysis of the various intermediate products at each stage in this process as well as final products, we have discovered that the reduced crude actually contains a substantial amount of low melting point microcrystalline waxes, i. e. waxes melting at about 105° F. or in the range of about 95° to 115° F. These low melting waxes are unique in character because of the tenacity with which they hold oil. In the above described refining process, it was found that this low melting point microcrystalline wax is largely removed from the bright stock in the oil associated with the crude petrolatum base but that it was substantially entirely removed from the petrolatum base when the latter was subjected to deoiling so that the final petrolatum contained substantially no low melting microcrystalline wax. In a particular example, a petrolatum base charged to the deoiling and decolorizing step contained 52.3% of oil, 12.7% of low melting point microcrystalline wax and 35% of high melting point microcrystalline wax (melting above 130° F.). The first wash oil obtained by recrystallization and settling was found to contain about 27% low melting point microcrystalline wax and the wax after this first washing step contained only 8.8% of such low belting point microcrystalline wax. The oil from the second washing step contained about 20% microcrystalline wax so that the rewashed wax contained less than 6%. A third wash oil likewise contained about 20% low melting point microcrystalline wax and after three washings, the wax contained less than 2½% of the low melting point microcrystalline wax. Repeated recrystallization and washing thus removes substantially all of the low melting microcrystalline wax so that the final petrolatum product consisted essentially of only high melting point microcrystalline waxes and oil. No microcrystalline wax was separable from the bright stock by chilling in hexane solution, but as much as 5% of low melting microcrystalline wax was separated therefrom by use of a hexane-acetone solvent.

Heretofore the oil separated from crude petrolatum base in the deoiling step was either added back to bright stock or discarded to gas oil charged to catalytic cracking operations. The first of these expedients was objectionable because as little as 2% of the wash oil when added to zero pour bright stock was found to raise its pour point from 0° F. to about 20° F., while when 10% of the wash oil was added to zero pour bright stock, the pour point of the resulting blend was raised to about 40° F. In view of the remarkable and valuable properties of the low melting waxes, they should certainly not be employed as a catalytic cracking charge.

The low melting microcrystalline wax may be separated from the wash oil obtained from the deoiling of crude petrolatum base by various dewaxing processes. We have found that when such oil is admixed with about 10 volumes of a treating agent consisting of about equal parts of hexane and acetone, the mixture is heated to effect complete solution and then cooled to a temperature in the range of 0° F. to −50° F., substantially all of the low melting point microcrystalline waxes may be separated from oil. For best results, a low temperature fractionation at a temperature of the order of −40 to −50° F. is first effected in order to remove substantially all of the oil from the microcrystalline waxes and the deoiled wax is then subjected to a second fractionation at a somewhat higher temperature of the order of −20° F. to +20° F. (e. g. 0° F.) to effect separation of the low melting point microcrystalline waxes from any high melting point microcrystalline wax which may be present. The above procedure may be modified by employing other light hydrocarbons of the C_3 to C_8 boiling range instead of hexane and other polar solvents, particularly low boiling ketones, such as methyl ethyl ketone, methyl butyl ketone, etc., instead of acetone. The proportions of the treating agent may be altered to some extent although it should contain at least 30%, but not more than 90%, of the paraffinic component. The low melting microcrystalline waxes may also be recovered to a considerable extent from the wash oil separated from crude petrolatum base by subjecting said oil to known dewaxing processes, such as propane dewaxing, benzol-acetone dewaxing, benzol-methyl ethyl ketone dewaxing, etc.

While wash oil from the refining of crude petrolatum base is the richest source of our low melting point microcrystalline wax, it should be understood that such low melting microcrystalline wax may be obtained from bright stock itself by the methods hereinabove described, thus improving the pour point of the bright stock and simultaneously obtaining the valuable low melting microcrystalline wax.

It should be emphasized that our low melting microcrystalline wax is substantially free from resins or other wax crystallization modifiers. It is a product which is unique in petroleum refinery practice and which is of great value in improving the quality of petrolatums generally and particularly in improving the quality of trough greases.

An outstanding problem in the manufacture of petrolatums and particularly in the manufacture of trough greases, has been the tendency of such products to bleed. This bleeding tendency of petrolatum is discussed at length by Kinsel and Phillips in Petroleum Refiner, vol. 27, No. 8, page 98 et seq. (August 1948), wherein tests are set forth to show the bleeding tendencies of petrolatums. The so-called crater test is perhaps the most significant in trough greases; in this test, samples are poured into cans about 3 inches in diameter by 2 inches deep, the petrolatum is allowed to congeal, craters are formed in each can by twisting a wedged-shaped spatula therein and the samples are allowed to remain in an oven kept at about 30° C. for periods of 24 to 96 hours or more, the separated oil which accumulates in the

crater being measured to determine the amount of bleeding. We have discovered that when a trough grease consisting of about 15% of a high melting microcrystalline wax (oil-free white petrolatum) and about 85% white oil which gave extensive bleeding when subjected to this crater test, was modified by adding 10% of 105° F. melting point microcrystalline wax, the resulting trough grease was markedly improved in gloss and luster, was characterized by much greater smoothness and lack of graininess and showed no bleeding whatsoever even after a long storage period.

The amount of low melting microcrystalline wax which should be added to the petrolatum or trough grease will, of course, depend to a certain extent on the particular specifications which must be met and on the character of the petrolatum employed as determined by its source. Petrolatums produced from non-asphaltic light colored Pennsylvania crudes which do not require much, if any, washing in its course of manufacture, may require very little low melting point microcrystalline wax, but even the best of the petrolatums from Pennsylvania crudes are improved in appearance, smoothness and resistance to syneresis or bleeding by the addition of as little as 2 or 3% of our low melting microcrystalline wax. Petrolatums produced from Mid-Continent or other crudes which require deasphalting and deresining and which require more solvent washing to obtain the desired light color, may be improved in appearance, smoothness and resistance to syneresis so that they are equal or superior to the best Pennsylvania crude petrolatums by adding large amounts of the microcrystalline wax. The amounts of the low melting point microcrystalline wax in this case is usually in the range of 5 to 25% or more by weight based on the total petrolatum compositions or trough greases to which they are added, 10% of added low melting point microcrystalline wax being usually sufficient to convert an inferior trough grease produced from Mid-Continent crude into a trough grease which is superior to the best producible from Pennsylvania crude.

The effectiveness of various amounts of our low melting microcrystalline wax in preventing bleeding (crater test) when added to petrolatums produced from Mid-Continent petroleum is shown in the following tests:

Microcrystalline wax was added to a trough greast prepared from Mid-Continent crude, the added microcrystalline wax being in the form of a 50% wax-50% oil mixture in amounts of 5%, 7.5%, 10%, 15%, 20% and 50% by weight of the trough grease, which gave a soft trough grease containing added microcrystalline wax in amounts of 2.5%, 3.75%, 5%, 7.5%, 10% and 25% respectively. The control sample of soft trough grease was grainy and showed loss of gel structure accompanied by excessive bleeding in the test. The sample containing 2.5% of added wax exhibited some improvement with respect to bleeding. The sample to which 3.75% wax was added showed distinct improvement in structure and still less bleeding than the sample to which 2.5% wax was added. Samples to which wax was added in amounts of 5% and greater, up to 25%, showed no bleeding, improved gloss and sheen, and absence of graininess. The addition of the wax in the form of a 50%–50% mixture of wax and oil resulted in the incorporation of added oil to the grease. Notwithstanding this addition of oil, the bleeding characteristics of the grease were overcome.

As above stated, trough greases contain more white oil than ordinary petrolatums and our invention is, therefore, particularly applicable in trough grease compositions because it enables the incorporation of more oil into the compositions than could otherwise be tolerated without encountering any syneresis difficulties. Advantageous results, however, may be obtained by incorporating about 2 to 25% of our low melting microcrystalline wax in crude petrolatum marketed for veterinary purposes, ordinary grades of petrolatum and refined petrolatums marketed for pharmaceutical purposes. In all cases, the added low melting microcrystalline wax tends to prevent oil separation even on prolonged storage at relatively high temperatures, i. e. at temperatures of about 30° C. or 90° F., which approximates ordinary skin temperatures (cosmetic use).

The addition of the defined amounts of low melting point microcrystalline wax to trough greases does not seriously affect any other properties of the trough grease. The white oil component of the trough grease should, of course, meet U. S. Pharmacopoeia specifications and is simply a highly refined white mineral oil usually having a viscosity at 100° F. in the range of 85 to 300 seconds Saybolt or more (less highly refined oils may be employed where the improved petrolatum is to be used for other purposes). The ASTM melting point of trough greases should be in the range of about 100 to about 115° F. They should have a flash point upwards of 350° F. Their penetration at 77° F. (30 gram cone) may range from about 150 for hard greases to as much as 350 to 400 in the case of soft greases. The viscosity at 210° F. should be in the range of about 35 to 50 seconds Saybolt. The addition of our low melting point microcrystalline wax to a trough grease formulation or in fact to any petrolatum does not present any problem from the standpoint of existing specifications, but after such addition, the product is found to have a more pleasing gloss and luster, is found to be much more smooth and less grainy, and is found to be free from any tendency toward syneresis or leaking as measured by the crater test. It will thus be seen that we have accomplished the objects of our invention.

We claim:

1. A composition of matter consisting essentially of microcrystalline wax melting in the range of 120° F. to 165° F. and a refined mineral oil in such proportions that the oil will constitute about 50% to 85% of this mixture and added microcrystalline wax melting in the range of about 95° F. to 115° F. in an amount in the range of about 2 to 25 weight per cent based on the total mixture, both of said microcrystalline waxes being further characterized by having boiling ranges above 900° F. on a true boiling point basis.

2. The method of claim 1 wherein both microcrystalline waxes are white waxes and the refined mineral oil is a white oil.

3. A trough grease consisting essentially of approximately 85% white mineral oil and about 15% of an oil-free white, high melting, microcrystalline hydrocarbon wax melting in the range of about 120° F. to 165° F. and containing an added amount of a microcrystalline wax melting in the range of about 95° F. to 115° F., said added amount being in the range of 2 to 25 weight per cent based on the total of the white oil and oil-free high melting point microcrystalline wax, and both

of said microcrystalline waxes being further characterized by having boiling ranges above 900° F. on a true boiling point basis.

4. The method of improving the texture and anti-syneresis properties of a petrolatum containing more than 80 per cent by weight of white mineral oil, which method comprises adding to said petrolatum a small amount of a low melting microcrystalline wax having a melting point in the range of about 95° F. to 115° F., and boiling, on a true boiling point basis, in the range of 900° F. to 1150° F.

5. The method of claim 4 wherein the amount of added low melting microcrystalline wax is in the range of about 2 to 25% of the total petrolatum mixture.

6. The method of claim 4 wherein the amount of added low melting microcrystalline wax is approximately 10% by weight of the total petrolatum mixture.

7. A composition of matter consisting essentially of a refined mineral oil having a viscosity in the range of 85 to 300 second Saybolt at 100° F., a high melting point microcrystalline wax having a melting point above 120° F. and a low melting point microcrystalline wax having a melting point below 115° F. and boiling in the range of about 900 to 1150° F. on a true boiling point basis, the refined mineral oil constituting more than 80 but not substantially more than 90 weight per cent of combined mineral oil and high melting microcrystalline wax, and the low melting microcrystalline wax constituting about 5 to 25 weight per cent based on the total mixture.

8. The composition of claim 7 wherein the refined mineral oil is a white oil and wherein said white oil and wax meet U. S. Pharmacopoeia requirements.

9. The composition of claim 7 wherein the resulting mixture is a trough grease having an ASTM melting point in the range of 100 to 115° F., a flash upwards of 350° F. and a penetration at 77° F. with a 30 gram cone in the range of about 150 to about 400.

10. An improved petrolatum which consists essentially of a viscous refined mineral oil, a high melting point microcrystalline wax and a low melting point microcrystalline wax, said high melting point microcrystalline wax having a melting point higher than 120° F. and being present in amounts in the range of 15 to 50 weight per cent of oil plus high melting wax components and the low melting microcrystalline wax melting below 115° F. and being present in amounts in the range of about 5 to 25 weight per cent based on the total mixture, both of said microcrystalline waxes being further characterized by having boiling ranges above 900° F. on a true boiling point basis.

11. The method of enhancing the gloss and luster of a petrolatum containing about 50 to 85 per cent of refined mineral oil, making it smoother and less grainy and making it substantially free from any tendency toward syneresis, which method comprises incorporating in said petrolatum a low melting point microcrystalline wax melting below 115° F. and boiling above about 900° F. on true boiling point basis, the amount of said low melting point microcrystalline wax being in the range of 5 to 25 weight per cent based on the total mixture and sufficient to enable microcrystalline wax in the petrolatum to hold oil with which it is associated in said petrolatum.

12. The method of making a petrolatum mixture from a reduced petroleum crude oil which is substantially free from asphalts and resins and from which components boiling up to 900° F. and including motor oil distillate have been distilled, which method comprises separating from said reduced crude a petrolatum mixture consisting essentially of microcrystalline waxes and oil, deoiling said mixture to obtain a substantially oil free microcrystalline wax having a melting point of at least about 120° F. and an oil containing microcrystalline waxes of lower melting point, separating from last named oil substantially oil-free microcrystalline wax having a melting point in the range of about 95 to 115° F., blending refined white mineral oil with said microcrystalline wax having a melting point of at least 120° F. in an amount to give a mixture containing about 50 to 90 weight per cent white mineral oil based on these two components and adding to these two components said microcrystalline wax having a melting point in the range of 95 to 115° F. in an amount in the range of 2 to 25 weight per cent based on the total mixture.

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