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AMIDOESTER WAXES AND METHOD OF FORMING

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9 Claims. (Cl. 260—404.5)

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This invention relates to amidoester waxes and the method of forming the same, and more particularly to a synthetic wax having very much the properties of carnauba wax.

A synthetic wax which would substitute carnauba was in the true sense is in great demand and as yet is commercially non-existent. In comparison with carnauba wax, the synthetic waxes to date fall short in several ways. Among these may be mentioned, solubility behavior, softening and melting range, gloss, hardness, toughness, and the ability to form tough or durable glossy films when rubbed and buffed onto a surface. The latter property, being especially important, is lacking in waxy compounds like the present amides, methylene diamides, hydrogenated glycerides, hydrocarbons, etc. Although the composition of carnauba wax is known at least in a general way, it is not practical to prepare a synthetic wax of the same composition as carnauba because the constituents are scarce and/or difficult to synthesize.

An object of this invention is to provide new synthetic waxes which tend to be non-crystalline and which possess the property of forming glossy films readily when rubbed onto a surface. A further object is to provide a method in which there is a controlled alteration of the molecular size and structure for obtaining non-crystalline waxes of different melting ranges and different degrees of hardness and toughness, while yet possessing the above-mentioned desirable characteristics of carnauba wax. A further object is to provide a method for producing waxes of the above characteristics having a melting range falling well within the commonly desired limits. A still further object is to provide a series of new synthetic waxes having the desired characteristics of carnauba wax and which form glossy films readily when rubbed onto a surface, and new and improved methods for forming such products. Other specific objects and advantages will appear as the specification proceeds.

The class of compounds which makes up the synthetic waxes of this invention are amidoesters. More specifically, these waxes are reaction products of (A) higher fatty acids and alkanolamines; and (B) higher fatty acids, alkanolamines, and polybasic acids or their ethyl esters. By higher fatty acids or "high molecular weight fatty acids," I mean fatty acids having from 10 to 26 carbon atoms. I prefer to employ fatty acids having from 10 to 22 carbon atoms. However, all of the

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fatty acids containing 10 or more carbon atoms give the desired new results set out herein, and such acids are available up to about 26 carbons in chain length.

In preparing (A) the amidoesters from the higher fatty acids and alkanolamines, the calculated quantities of fatty acid and alkanolamine (to give a complete reaction) are merely heated together (say about 150°–180° C.), preferably in an inert atmosphere and finally under reduced pressure (preferably about 5 to 15 millimeters of mercury). If desired, the temperature may be raised above 180° C. I find, however, that it is ordinarily unnecessary to go above this temperature and that there is no advantage in doing so. The following illustrates the formation of the simpler type (A) amidoesters:

(1)

$$RC(=O)OH + R'C(=O)OH + NH_2CH_2CH_2OH \longrightarrow RC(=O)NHCH_2CH_2OC(=O)R' + 2H_2O$$

(2)

$$RC(=O)OH + R'C(=O)OH + R''C(=O)OH + NH(CH_2CH_2OH)_2 \longrightarrow RC(=O)N(CH_2CH_2OC(=O)R')(CH_2CH_2OC(=O)R'') + 3H_2O$$

where R, R', and R'' are higher alkyl radicals and may or may not be the same.

The preparation of (B)—the amidoesters from the higher fatty acids, alkanolamines, and polybasic acids or their ethyl esters—is necessarily performed in two or more steps depending on the structural complexity of the final product. For the second type (B) of amidoesters the following illustrates their formation:

(1)

$$RC(=O)OH + NH_2CH_2CH_2OH \longrightarrow RC(=O)NHCH_2CH_2OH + H_2O$$

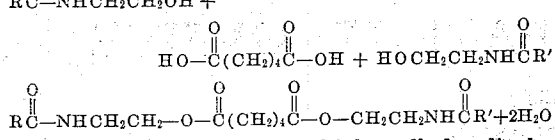
R being a higher alkyl radical — (Ethylolalkylamide)

(2)

$$2RC(=O)NHCH_2CH_2OH + HOC(=O)(CH_2)_4C(=O)OH \longrightarrow RC(=O)NHCH_2CH_2OC(=O)(CH_2)_4C(=O)OCH_2CH_2NHC(=O)R + 2H_2O$$

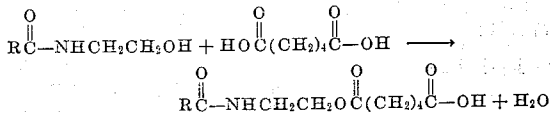
Where the adipic acid may be substituted by any polybasic acid or its ethyl ester. Equation 2 may be written thus:

(3)



R and R' being two different higher alkyl radicals. In order to increase chain length of the molecule to any predetermined extent reaction (2) is modified as follows:

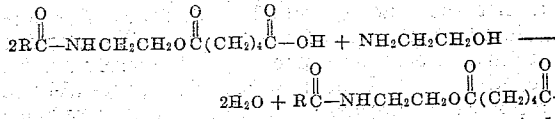
(4)



(4a)

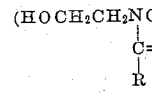
Two moles of the product (4a) may be "bridged" with 1 mole of an alkanolamine

(5)



or one mole of the product (4a) may be reacted with one mole of an alkanolamine and the resulting hydroxy compound again reacted mole per mole with a dibasic acid as shown in (4), etc., the process of alternate mole per mole reaction of alkanolamine and dibasic acid being repeated until it is desired to "bridge" the resulting hydroxyl or carboxyl compounds. If the last reactant in the chain lengthening process is an alkanolamine, thus giving rise to a compound with a terminal hydroxyl group, then such a compound is "bridged" by reacting two moles of it with one mole of dibasic acid. On the other hand, if the terminal group of the compound to be "bridged" is a carboxyl, then two moles of such a compound are reacted with one mole of an alkanolamine.

Dialkylolamides



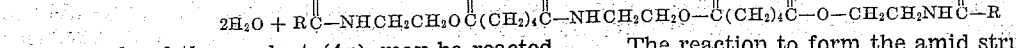
where R is an alkyl radical) when used instead of alkanolamines in the "bridging" or chain lengthening process impart translucency and lower melting properties to the resulting amidoesters. Increasing the chain length in general increases the toughness of the product. As may be seen from what has been stated above, one may use several different alkanolamines and alkylolamides, several different dibasic acids and several different higher fatty acids in making up one and the same lengthened and "bridged" amidoester.

Any of the high molecular weight fatty acids may be employed with satisfactory results. I have obtained especially good results with stearic acid, and also with palmitic acid. All of the fatty acids, containing 10 or more carbon atoms, give the desired new results set out herein. Such acids are available up to about 26 carbons in chain length.

My experimental results in carrying out the process described herein indicate that the mono and dialkanol amines containing at least 2 carbon atoms can be made to respond to the process to produce the waxy compounds which are the main purpose of the invention. In particular, the mono and diethanol amines have been found to give excellent results.

Any polybasic acid or its ethyl ester may be employed, and in the examples set out below, various specific acids and their ethyl esters are listed. All of the polybasic acids and their ethyl esters respond to give the new series of waxes having the desired characteristics mentioned, and particularly the characteristic of forming glossy films readily when rubbed onto a surface.

From what has been stated above, it can be seen that a considerable number of amidoesters can be readily prepared from relatively common starting materials. These amidoesters are all waxy compounds differing from each other in such physical properties as melting point, hardness, and toughness. The latter physical properties depend on the chemical composition, a factor which is readily controlled as described previously in this invention.



The reaction to form the amid structure takes place at temperatures above 140° C. and the reaction to form the ester structure takes place from about 140° C. upward, and it is usually necessary to employ temperatures in excess of 180° C. to complete the reaction. However, temperatures in excess of 240° C. are not recommended due to the likelihood of decomposition at such high temperatures. If desired, an inert atmosphere may be used in conducting the reaction, but this is not essential and, in most cases, may be dispensed with in commercial operations.

Specific examples of the process and of the product and of the series of products covered herein may be set out as follows:

EXAMPLE 1

The amidoester of stearic acid and ethanolamine

713.4 grams of stearic acid and 78 grams of ethanolamine (molecular proportions: 2 stearic acid, 1 ethanolamine) were mixed and heated (preferably with stirring) for 1¾–2 hours at 175–185° C. in an inert atmosphere. The mixture was then heated at 185–195° C. and 10–15 mm. pressure for 4 to 5 hours and cooled to 130–140° C. under vacuum before pouring out.

This product was hard, close grained, and light colored (light tan). It melted at 85–87° C. and formed a glossy film when rubbed onto a surface (such as brown paper).

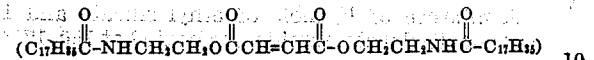
Ethylol stearamide, which was a starting material in the folowing examples, was prepared as follows:

Stearic acid (290 grams) was mixed with 80–90 cc. (an excess of the calculated) of ethanolamine. The mixture was heated for 2 hours at 180° C. in an atmosphere of nitrogen and then for 2–2½ hours at 160–200° C. and 10–15 mm. pressure to remove the unreacted ethanolamine. The product obtained was a soft light colored solid, melting at 94–96° C.

EXAMPLE 2

The amidoester of stearic acid, ethanolamine and maleic anhydride

Molecular proportions of the reactants represented in the final product were: Stearic acid 2, ethanolamine 2, maleic anhydride 1.

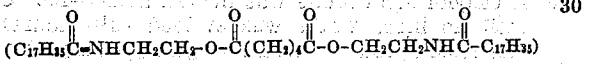


A mixture of 208.5 grams of ethylol stearamide and 31.3 grams of maleic anhydride was heated for 2 hours at 150–170° C. and 10–15 mm. pressure. Under these conditions of heating, a rapid reaction set in at 150° C. and the temperature was allowed to rise as the reaction rate decreased. After cooling to about 130° C. (under vacuum), the reaction product was poured into beakers to solidify. At room temperature, it was a reddish, fine-grained brittle wax which formed a glossy film when rubbed onto a surface. The melting point was 65–72° C.

EXAMPLE 3

The amidoester of stearic acid, ethanolamine and adipic acid

Molecular proportions of the reactants represented in the final product were: Stearic acid 2, ethanolamine 2, adipic acid 1.

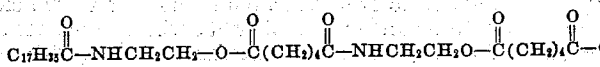


A mixture of 114 grams of ethylol stearamide and 24.5 grams (theoretical) of adipic acid was heated at a pressure of 10–15 mm. for 4 hours. The reaction progressed rapidly at 150° C., but the temperature was allowed to attain 180° C. within an hour and was maintained at 180–190° for the next two hours. It was then raised to 200°–220° C. for the remaining 2 hours. In order to remove any traces of oily and distillable by-products, the reaction mixture was heated at 190–220° C. for about 2 hours at 3 to 5 mm. pressure. After cooling to 130–140° C. under vacuum, the hot liquid was poured into beakers. At room temperature, the product was a tan colored, hard, fairly tough, fine grained and glossy wax which formed a glossy film when rubbed onto a surface. Melting temperature: softened some at 70° C. and liquified at 98–110° C.

EXAMPLE 4

The amidoester of stearic acid, ethanolamine and adipic acid

Molecular proportions of the reactants represented in the final product were: Stearic acid 2, ethanolamine 3, adipic acid 2.

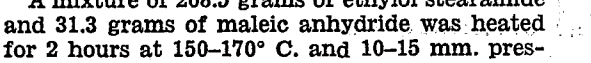


A mixture of equal molar proportions of ethylol stearamide and adipic acid was heated at 160–180° C. and 10 to 15 mm. pressure until bubbling ceased (about 2–3 hours). After cooling to 140° C. under vacuum, a half molar proportion of ethanolamine was added and the mixture was heated in an atmosphere of nitrogen (at atmospheric pressure) for 2 hours at 170–185° C. and then for 2 hours at 10–15 mm. pressure and 180–200° C. The reaction product was cooled to 130–140° C. in vacuo and poured into beakers. The wax thus obtained softened at 70–75°, liquified at about 100°, and resembled that of Example 3 in color, hardness, gloss, and the ability to produce a glossy film when rubbed onto a surface. However, it was somewhat tougher and finer grained (tending toward translucency) than the wax of Example 3.

EXAMPLE 5

The amidoester of stearic acid, ethanolamine and sebacic acid

Molecular proportions of the reactants represented in the final product were: Stearic acid 2, ethanolamine 2, sebacic acid 1.



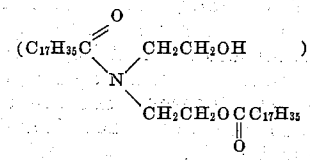
The procedure in this case was the same as that in Example 3, except that the adipic acid was substituted by an equal molar proportion of sebacic acid. The final (sebacic) product resembled the adipic product of Example 3 except that it was slightly lower melting and somewhat tougher.

EXAMPLE 6

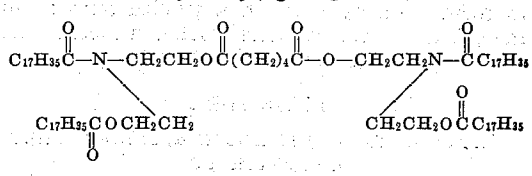
The amidoester of stearic acid, diethanolamine and adipic acid

Molecular proportions of the reactants represented in the final product were: Stearic acid 4, diethanolamine 2, adipic acid 1.

The first step in this process was the preparation of the monostearate of diethylol stearamide



The second step consisted of uniting or "bridging" two molecules of the above hydroxyamide ester with one molecule of adipic acid through the unreacted hydroxyl, giving:



Preparation of compound (A): A mixture of 2 moles of stearic acid and 1 mole of diethanolamine was heated, preferably in an inert atmosphere, for ½ hour at 140–160° C. After this, the heating was continued at 10–15 mm. pressure and 140–160° C. Although the reaction appeared to be completed after 1 hour, the process was continued for another hour with the temperature rising to 180° C. On cooling, there was obtained a tan colored semi-translucent, waxy solid, melting at 53–55° C.

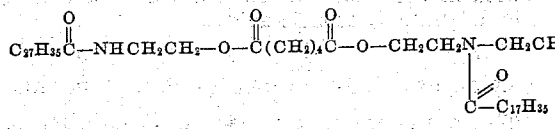
Preparation of compound (B): The reaction product (A) (1 mole) was mixed with ½ mole of adipic acid and heated at 10–15 mm. pressure. Water was rapidly evolved at 100–140° C. After heating at 100–140° C. for 1 hour, the temperature was raised to 170° C. during the second hour. Finally, the temperature was raised to 200° C. for ½ hour (till there was no more evidence of reaction). After cooling in vacuo to 100° C., the hot melt was poured into beakers. The product was a glossy, waxy solid of medium hardness and light tan color (quite translucent), melting

at 48–50° C., and formed a very glossy film when rubbed onto a surface.

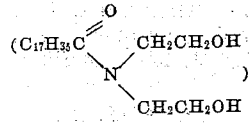
EXAMPLE 7

The amidoester of stearic acid, ethanolamine and diethanolamine and adipic acid

Molecular proportions of the reactants represented in the final product were: Stearic acid 3, ethanolamine 2, diethanolamine 1, adipic acid 2.



In this preparation, it was necessary to prepare diethylol stearamide



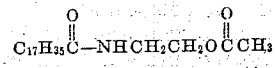
as well as the ethylol stearamide before hand. The diethylol stearamide was prepared by heating a mixture of equal molar proportions of stearic acid and diethanolamine in the same manner described under the preparation of ethylol stearamide.

A mixture of equal molar proportions of ethylol stearamide and adipic acid was heated at 160–175° C. and 10 mm. pressure until the bubbling ceased (about 1 hour required) and then at 190–200° C. for another half hour. After cooling to 140° C. in vacuo, a half molar proportion of diethylol stearamide was added, and the resulting mixture was heated at 190–200° C. and 10–15 mm. pressure for 4 to 5 hours to effect a "bridging" between the free adipic carboxyls.

The resulting product was cooled as described in previous examples. It resembled the product obtained in Example 6 in gloss and in its ability to form a glossy film when rubbed onto a surface, but it was a little darker in color, less translucent, and liquefied at 75–85° C.

EXAMPLE 8

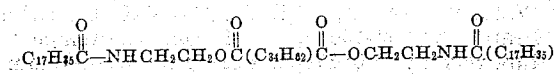
The amidoester of stearic acid, ethanolamine and acetic acid



A mixture of equal molar proportions of ethylol stearamide and acetic anhydride was heated at 140° C. After ½ hour, a vacuum (10–15 mm. pressure) was applied and the temperature was gradually raised to 135° C. and maintained thus until the acetic acid liberated in the reaction was distilled out (about 1 hour). The cooled product was a tan colored, waxy solid, melting at 73–77° C., but it was considerably softer than that obtained in Example 1.

EXAMPLE 9

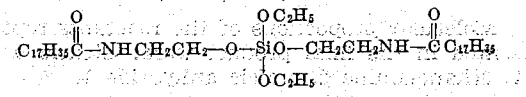
The amidoester of stearic acid, ethanolamine and dimerized linoleic acid



A mixture of ½ mole of dimerized linoleic acid and 1 mole of ethylol stearamide was heated at 160–165° C. and 10–15 mm. pressure until there was no further evidence of the evolution of water (about 6 hours). The cooled product was a light brown, semi-translucent wax, melting at 70–75° C.

EXAMPLE 10

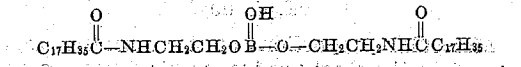
The amidoester of stearic acid, ethanolamine and diethoxysilicic acid



A mixture of ½ mole of ethyl silicate and 1 mole of ethylol stearamide was heated at 150–175° C. until there was no more evidence of the evolution of ethyl alcohol (about 2 hours). The cooled product resembled the adipic product of Example 3 in color, hardness, toughness, gloss, film-forming properties, and melting point.

EXAMPLE 11

The amidoester of stearic acid, ethanolamine and boric acid



A mixture of ½ mole of boric acid and 1 mole of ethylol stearamide was heated at 145–150° C. until no more water was evolved (2½ hours). The cooled product was a very glossy, orange-tan, brittle wax, melting at 110–140° C. It formed a glossy film when rubbed onto a surface.

While in the foregoing specification, I have set forth specific steps in great detail for the purpose of illustrating certain embodiments of the invention, it will be understood that such details may be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

1. In a process for preparing an amidoester wax product, the steps of condensing about a 1 to 1 molar ratio of a saturated monobasic fatty acid containing an even number of carbon atoms within the range from 10 to 26 carbon atoms with an amine selected from the group consisting of mono and dialkanolamines containing at least 2 carbon atoms by heating said reactants to about 140 to 240° C. to form an alkylolamide, and then reacting about a 2 to 1 molar ratio of the alkylolamide with an aliphatic dibasic acid by heating said second-mentioned reactants to about 180 to 240° C. to complete the reaction.

2. In a process for preparing an amidoester wax product, the steps of condensing about a 1 to 1 molar ratio of a saturated monobasic fatty acid containing an even number of carbon atoms within the range from 10 to 26 carbon atoms with an amine selected from the group consisting of mono and diethanol amines by heating said reactants to about 140 to 240° C. to form an alkylolamide, and then reacting about a 2 to 1 molar ratio of the alkylolamide with an aliphatic dibasic acid by heating said second-mentioned reactants to about 180 to 240° C. to complete the reaction.

3. In a process for preparing an amidoester wax product, the steps of condensing about a 1 to 1 molar ratio of stearic acid with an amine selected from the group consisting of mono and diethanolamines by heating said reactants to about 140 to 240° C. to form an alkylolamide, and then reacting about a 2 to 1 molar ratio of the alkylolamide with an aliphatic dibasic acid by

heating said second-mentioned reactants to about 180 to 240° C. to complete the reaction.

4. In a process for preparing an amidoester wax product from a saturated monobasic fatty acid containing an even number of carbon atoms within the range from 10 to 26 carbon atoms, the step of reacting an alkylolamide formed from said fatty acids and an amine selected from the group consisting of mono and diethanolamines with an aliphatic dibasic acid in a 2 to 1 molar ratio by heating said reactants to about 180 to 240° C. to complete the reaction.

5. A product produced in accordance with the process set out in claim 1.

6. In a process for preheating an amidoester wax product, the steps of condensing about a 1 to 1 molar ratio of a saturated monobasic fatty acid containing an even number of carbon atoms within the range from 10 to 26 carbon atoms with an amine selected from the group consisting of mono or dialkanolamines containing at least 2 carbon atoms by heating said reactants to about 140 to 240° C. to form an alkylolamide, condensing about a 1 to 1 molar ratio of said alkylolamide with an aliphatic dibasic acid to form a carboxyl compound by heating said reactants to about 140 to 240° C., and then condensing about a 2 to 1 molar ratio of said carboxyl compound with an amine selected from the group consisting of mono and dialkylanolamines containing at least 2 carbon atoms by heating said reactants to about 140 to 240° C. to form an amidoester wax product.

7. In a process for preparing an amidoester wax product, the steps of condensing about a 1 to 1 molar ratio of a saturated monobasic fatty acid containing an even number of carbon atoms within the range from 10 to 26 carbon atoms with an amine selected from the group consisting of mono and diethanolamines by heating said reactants to about 140 to 240° C. to form an alkylolamide, containing about a 1 to 1 molar ratio of said alkylolamide with an aliphatic dibasic acid to form a carboxyl compound by heating said reactants to about 140 to 240° C., and then condensing about a 2 to 1 molar ratio of said carboxyl compound with an amine selected from the group consisting of mono or diethanolamines by heating said reactants to about 140 to 240° C. to form an amidoester wax product.

8. In a process for preparing an amidoester wax product, the steps of condensing about a 1 to 1 molar ratio of stearic acid with an amine selected from the group consisting of mono and diethanolamines by heating said reactants to about 140 to 240° C. to form a alkylolamide, condensing about a 1 to 1 molar ratio of said alkylolamide with an aliphatic dibasic acid to form a carboxyl compound by heating said reactants to about 140 to 240° C., and then condensing about a 2 to 1 molar ratio of said carboxyl compound with an amine selected from the group consisting of mono and diethanolamines by heating said reactants to about 140 to 240° C. to form an amidoester wax product.

9. A product produced in accordance with the process set out in claim 6.

OTTO TURINSKY.

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