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3,035,070

# DIALKYLPOLYAMINOPOLYALKALENE AMIDES

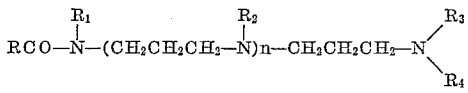
Joseph Emmett Carpenter, Thatcher, Ariz., and Edwin Ralph Kolodny, Stamford, Conn., assignor to American Cyanamid Company, New York, N.Y., a corporation of Maine

No Drawing. Original application Sept. 11, 1957, Ser. No. 683,226, now Patent No. 2,737,106, dated May 17, 1960. Divided and this application Feb. 26, 1960, Ser. No. 11,145

3 Claims. (Cl. 260—404.5)

This invention relates to certain dialkylpolyaminopolyalkalene amides, which have excellent stability at elevated temperatures, both in an asphalt composition alone and in an asphalt composition in contact with both alkaline and acid aggregate.

More specifically, the compounds are of the general formula:



where the RCO is an acyl group derived from a carboxylic acid of from 12 to 20 carbon atoms which may be of the saturated or unsaturated fatty acid series, and particularly naturally occurring acids and their mixtures, $R_1$ and $R_2$ are hydrogen or 1 to 4 carbon alkyl radicals, $R_3$ and $R_4$ are alkyl radicals of from 1 to 4 carbon atoms, and $n$ is a small whole number, not less than 1 nor more than 4; and the fatty acid and rosin acid salts of these amides.

The problem of securing a satisfactory bond between bituminous compositions and the various surfaces to which they are applied in industrial operations, particularly stony aggregate in road building, is well recognized. Many patents have issued on various bonding agents, of which the most effective have generally been cationic surface active agents. Among the better of these are included aminoalkyl amides and polyaminoalkyl amides, sometimes used also as their carboxylic acid salts. Most of these products are effective in causing the adherence of the bituminous compositions to aggregates in certain instances, but possess serious shortcomings for general purpose use.

It has been well recognized that it is desirable that the bituminous composition containing the additive should be storage stable even at elevated temperatures of the nature of 350° F., and preferably even higher, inasmuch as asphalt is commonly stored hot for periods of a week or more prior to use. It is also desirable that the bituminous composition containing the additive should adhere to wet as well as to dry aggregate and to cold as well as to hot aggregate. It has also been recognized that there are various classes of aggregate, some of which are acidic in character, and some of which are basic in character, and that it would be desirable to provide a single all-purpose additive which would be effective with either of these or with mixtures of the two.

The present compounds are effective asphalt additives. Their use as such is described in more detail in application 683,226, filed September 11, 1957, entitled "Dialkylpolyaminopolyalkalene Amides as Asphalt Antistripping Agents," now U.S. Patent 2,937,106, dated May 17, 1960, of which this application is a division.

The novel compounds of the present invention are essentially the reaction product of a dialkylpolyaminopolyalkylene amine, and a fatty acid having from 12 to 20 carbon atoms. The fatty acids from natural sources such as tall oil, fish oil, coconut oil, and the like, are particularly useful commercially. Where price permits, the more or less pure fatty acids such as oleic or linoleic acid are



entirely effective and completely satisfactory. The fatty acids need not be used in pure form, and commercially it is found particularly advantageous to use crude tall oil, which, in addition to the fatty acids, also contains a certain amount of rosin acid. While not necessary, the rosin acid may be permitted to remain in the additive and form a salt with the amine groups, and in fact, it is also possible to use a sufficient excess of fatty acid so that at least part of the amine groups form salts with the fatty acid.

While the compounds of this invention contain at least two amino groups in addition to the nitrogen present in the amide group, more amino groups may be present.

The polyamine starting material is conveniently prepared by adding a dialkylaminoalkylamine to acrylonitrile and hydrogenating the product, for example, with Raney nickel catalyst, preferably in the presence of ammonia, which converts the nitrile groups to primary amine groups. The product thus obtained, starting with a dimethylaminopropylamine would be a dimethylaminopropylaminopropylamine. Other dialkylamino starting materials may be used containing up to 4 carbon atoms in the alkyl groups. Mixtures may be used as well as compounds in which the alkyl groups are not necessarily the same. Dialkylaminopropylaminopropylamine may be reacted with additional acrylonitrile and the product again hydrogenated to add an additional propylamino moiety to the chain. The cost of this reaction is such that the dialkylaminopropylaminopropylamines will generally be preferred commercially over longer chain products containing more propylamino groups, but the longer chains are very useful where the cost structure is such as to permit their use.

The intermediates prepared as above contain secondary amino groups along the chain. Other useful products result when these secondary amine groups are alkylated by alkyl groups of 1 to 4 carbon atoms, and the alkylation may be performed either before or after the reaction of the intermediate polyamine with a fatty acid. One simple method is to add an aldehyde or ketone of not more than 4 carbon atoms to the adduct of acrylonitrile and dialkylaminopropylamine. The secondary amino group will be reductively alkylated simultaneously with the hydrogenation of the nitrile group. Reductive alkylation may also be applied to the polyamine after reaction with the fatty acid. Alternately, special methods of alkylation, specifically methylation, may be applied, as for example by the use of formaldehyde and formic acid as described in Example 11 below.

The present novel materials are most conveniently added to or incorporated in a bituminous component before it is mixed with aggregate, as, for example, they may be added to molten asphalt or to cut back asphalt. However, if desired the dialkylpolyaminopolyalkalene amides may be added to the mixer in which the bituminous material and the mineral aggregate are being mixed, and, in the case of asphalt emulsions, the dialkylpolyaminopolyalkalene amides may be added to the emulsion after it has been produced, or to the bituminous component of such emulsions before emulsification.

In addition to their use as asphalt additives, the present novel dialkylpolyaminopolyalkylene amides are useful as cationic surface active agents, and may be used as flotation reagents and additionally possess fungicidal activity.

The invention is further illustrated by the following examples in which parts are by weight, unless otherwise stated:

## EXAMPLE I

*Dimethylaminopropylaminopropylamine*

Dimethylaminopropylamine is reacted with an equal

molecular proportion of acrylonitrile, using cooling to prevent the reaction from getting out of control, and the resultant product is hydrogenated at a temperature between 90 and 120° C. at a pressure of 2000 lbs. per square inch with Raney nickel catalyst in the presence of ammonia. After substantially the theoretical uptake of hydrogen has occurred, the hydrogenation product is stripped of a minor proportion of low-boiling components by vacuum distillation at 25 mm. Hg to a final pot temperature of 110° C.

The residual product is dimethylaminopropylaminopropylamine as a colorless liquid, with a sharp ammoniacal odor.

## EXAMPLE 2

### *Distilled Tall Oil and Dimethylaminopropylaminopropylamine*

100 parts of distilled tall oil containing 0.25 equivalent of fatty acids per 100 grams, available as a commercial product, is mixed with 40.8 parts of dimethylaminopropylaminopropylamine produced as in Example 1. The mixture is heated in a reactor with a fractionating column and distillation condenser attached. The temperature is held at 150–160° C. until most of reaction occurs. The reaction is substantially complete after 1½ hours. The temperature is then raised to cause distillation of water formed in the reaction, and heating is dicontinued at 180° C. The product is a reddish, somewhat viscous liquid obtained in a yield of 135 parts. It is ready for use as an asphalt additive without further treatment.

## EXAMPLE 3

### *Crude Tall Oil and Dimethylaminopropylaminopropylamine*

The procedure of Example 2 is repeated using 40.8 parts dimethylaminopropylaminopropylamine and 156 parts of a crude tall oil containing 0.25 equivalent of fatty acids. The product is darker and less pure than obtained from using distilled tall oil as a starting material, and may be used as an asphalt additive without further refining.

## EXAMPLE 4

### *From Fish Oil*

The procedure of Example 2 is repeated, using an equivalent molecular proportion of a fish oil. The product is similar in appearance.

## EXAMPLE 5

### *From Coconut Oil*

The procedure of Example 2 is repeated, using an equivalent molecular proportion of coconut oil. The product is similar in appearance.

## EXAMPLE 6

### *From Oleic Acid*

10 mols of dimethylaminopropylaminopropylamine is mixed with 10 mols of oleic acid in a reaction vessel equipped with a fractionating column and condenser. The mixture is heated until the theoretical amount of water is distilled over. The resulting product is dimethylaminopropylaminopropyl oleamide.

## EXAMPLE 7

### *From Linoleic Acid*

The procedure of Example 2 is repeated, using 50 mols of linoleic acid and 50 mols of dimethylaminopropylaminopropylamine. The mixture is heated in a reactor equipped with a fractionating column and a distillation condenser, and the water which is eliminated is collected. After substantially all of the theoretical amount of water has been collected the mixture is allowed to cool and the thus produced dimethylaminopropylaminopropyl linoleamide is then ready for used as an asphalt additive.



## EXAMPLE 8

### *Dimethylaminopropylaminopropylaminopropylamine*

The product of Example 1 is reacted with an equal molecular proportion of acrylonitrile, cooling to prevent the reaction from getting out of control, and the resultant is then hydrogenated at between 90 and 120° C. and 2000 lbs. per square inch with Raney nickel catalyst in the presence of ammonia until substantially the theoretical uptake of hydrogen has taken place. The hydrogenation product is stripped of low boilers by vacuum distillation. The product obtained is dimethylaminopropylaminopropylaminopropylamine.

## EXAMPLE 9

### *Tall Oil and Dimethylaminopropylaminopropylaminopropylamine*

The product of Example 8 is reacted with distilled tall oil following the procedure of Example 2, correcting for the higher molecular weight of the amine. A substantially similar appearing product is obtained which is equally satisfactory as an asphalt additive.

## EXAMPLE 10

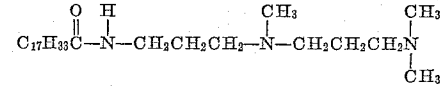
### *Oleic Acid and Dimethylaminopropylaminopropylaminopropylamine*

The procedure of Example 6 is repeated, using the dimethylaminopropylaminopropylaminopropylamine of Example 8. An excellent asphalt additive is obtained.

## EXAMPLE 11

### *Methylation of Dimethylaminopropylaminopropyl Oleamide*

423 parts of the product from Example 6 is heated under reflux for 4 hours with 100 parts 37% formalin, 51 parts 88% formic acid and 400 parts ethanol, at which time carbon dioxide evolution is complete. The ethanol is distilled off, the residue washed once with concentrated sodium hydroxide solution, and allowed to stand overnight over solid sodium hydroxide. The decanted viscous liquid is



## EXAMPLE 12

### *Diethylaminopropylaminopropylamine*

Diethylaminopropylamine is reacted with an equal molecular proportion of acrylonitrile following the procedure set forth in Example 1. There is obtained diethylaminopropylaminopropylamine.

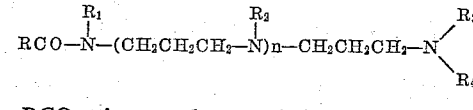
## EXAMPLE 13

### *Diethylaminopropylaminopropyl Oleamide*

The product of Example 12 is reacted with a molecular proportion of oleic acid using the procedure of Example 6. There is obtained diethylaminopropylaminopropyl oleamide.

Having described certain embodiments thereof as our invention, we claim:

1. A dialkylaminopolyamine of the formula:



where RCO— is an acyl group derived from a carboxylic acid selected from the group consisting of $C_{12}$ to $C_{20}$ saturated and unsaturated fatty acids, and mixtures thereof, $R_1$ and $R_2$ are radicals selected from the group consisting of hydrogen and 1 to 4 carbon alkyl radicals, $R_3$ and $R_4$ are 1 to 4 carbon alkyl radicals, and $n$ is a small whole number not less than 1 and not more than 4; and

its $C_{12}$ to $C_{20}$ saturated and unsaturated fatty acid and rosin acid salts.

2. A dimethylaminopropylaminopropyl amide of a 12 to 20 carbon atom fatty acid of the formula:

$$RCO—NH—CH_2CH_2CH_2—NH—CH_2CH_2CH_2—N—(CH_3)_2$$

where RCO— is an acyl group derived from a carboxylic acid selected from the group consisting of $C_{12}$ to $C_{20}$ saturated and unsaturated fatty acids, and mixtures thereof, and its $C_{12}$ to $C_{20}$ saturated and unsaturated fatty acid and rosin acid salts.



3. The compound of the formula:

$$RCO—NH—CH_2CH_2CH_2—NH—CH_2CH_2CH_2—N—(CH_3)_2$$

where RCO— represents the acyl group derived from tall oil fatty acids.

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