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HEAT TREATED REACTION PRODUCTS OF N-ALKYLAMINOPROPYL-γ-HYDROXYBUTYRAMIDES

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The present invention relates to heat treated reaction products of N-alkylaminopropyl-γ-hydroxybutyramides having varied industrial uses and to the process of preparing the same.

An object of the present invention is to provide a new and useful class of products obtained by the heat treatment of the reaction products of N-alkylaminopropyl-γ-hydroxybutyramides.

A further object is to provide a process of preparing the said products.

Other objects and advantages will become evident from the following description.

We have found that by heat treating the reaction product of a γ-lactone with an alkyl diamine at a temperature ranging from 170° to 250° C. and a reduced pressure, a product is obtained which is particularly useful in a variety of industrial applications, particularly as corrosion inhibitors of ferrous metals that are normally exposed to the deleterious action of water, air, acid and brines. In addition, they are particularly useful in the application to metals as slushing compounds and as oil well casing and pipeline inhibitors, as will be shown hereinafter.

The reaction products of N-alkylaminopropyl-γ-hydroxy-butyramides which are subjected to the heat treatment of the present invention are obtained by heating to approximately 90–100° C. 1 mole of a γ-lactone, such as either γ-butyrolactone or γ-valerolactone with 1 mole of an alkyl diamine having the following general formula:

$$RNHCH_2CH_2CH_2NH_2$$

wherein R represents at least one alkyl group containing from 8 to 23 carbon atoms, e.g. octyl, decyl, lauryl, myristyl, palmityl, stearyl, arachidyl, behenyl, oleyl, linoleyl, eleostearyl, linolenyl, tetracosanyl, etc. and mixtures thereof derived from fatty acids, e.g. coconut fatty acid, tallow fatty acid, soya fatty acid, etc., all of which are commercially available (for example, under the brand name of "Duomeens").

As illustrative examples of the alkyl diamines characterized by the foregoing general formula and wherein R is a straight alkyl chain or a mixture of alkyl groups of from 8 to 23 carbon atoms, the following may be mentioned:

N-octylpropylene diamine
N-decylpropylene diamine
N-dodecylpropylene diamine
N-undecylenylpropylene diamine.
N-tetradecylpropylene diamine
N-octadecylpropylene diamine
N-octadecadienylpropylene diamine
N-oleylpropylene diamine
N-elaidylpropylene diamine
N-tetracosanylpropylene diamine

The following are illustrative examples of mixed alkyl diamines wherein R consists of a mixture of alkyl groups of from 8 to 23 carbon atoms:

Duomeen S wherein R is an amine residue derived from soybean acids containing the following components:

	Percent
Oleyl	35
Stearyl	10
Linoleyl	45
Palmityl	10

Duomeen C wherein R is an amine residue derived from coconut fatty acids:

Octylamine	8
Decylamine	9
Dodecylamine	47
Myristyl	18
Palmityl	8
Stearyl	5
Linoleyl	5

Duomeen T:

Tetradecylamine	2
Hexadecylamine	24
Octadeylamine	28
Octadecenylamine	46

Duomeen 12:

Decylamine	2
Dodecylamine	95
Tetradecylamine	3

The straight chain alkyl diamines wherein R is an alkyl of from 8 to 23 carbon atoms are readily obtained by the reaction of a primary amine with acrylonitrile to give the corresponding cyanoethyl alkylamine. Hydrogenation of these products results in fatty diamines containing both primary and secondary amino groups. (See "Preparation of Various Complex Aliphatic Amines" (G. B. Bachman and R. L. Mayhew), The Journal of Organic Chemistry, vol. 10, No. 3, 1945.)

The heat treatment, which is an essential of the instant invention and which is hereafter exemplified, is usually conducted at pressures below atmospheric. While it is possible to operate within a wide range of reduced pressure, the preferred pressure range is 10 to 50 mm. Hg absolute. Most of the experiments were actually performed at 25 mm., however, it must not be concluded that this is necessarily the optimum pressure, other pressures are also quite operable.

The following examples will illustrate the preparation of the reaction products of γ-lactones with the alkyl diamines of the above general formula followed by their heat treatment into new compositions and the applications thereof.

EXAMPLE I

½ mole (93.1 grams) of N-octylpropylene diamine was charged to a 500 ml. flask equipped with a thermometer, stirrer and downward condenser to vacuum take-off. The charge was heated at 95–100° C. and 60 mm. of mercury pressure for ¼ hour to remove the water. ½ mole (43.0 grams) of γ-butyrolactone added after releasing the vacuum and the reaction mixture held at 95–100° C. for 2¼ hours. A vacuum of 25 mm. was then applied and the temperature raised to and held at 195–235° C. for 3 hours. The final product was a dark liquid soluble in light mineral oil. The total amine content was found to be .00740 mole/gram and the hydroxyl number

$$51.5=\frac{\text{mg. KOH}}{\text{grams}}$$

EXAMPLE II

½ mole (201.0 grams) of aminopropylsoyamine (Armour's Duomeen S) was charged to a 500 ml. flask equipped with a thermometer, stirrer and downward condenser to vacuum take-off. The charge was heated at 95°–100° C./60 mm. for ¼ hour to remove low boiling amines and water. ½ mole (43.0 grams) of γ-butyrolactone were added after releasing the vacuum and the reaction mixture held at 95–100° C. for 2¼ hours. The total amine content was found to be 0.00201 mole/gram and the hydroxyl number

$$112=\frac{\text{mg. KOH}}{\text{grams}}$$

A vacuum of 25 mm. was then applied and the temperature raised to and held at 195–235° C. for 3 hours. A total of 50.0 grams of low boiling material was distilled off. The final product was an amber liquid which was soluble in mineral oil 65/75 Carnation-Sonneborne). The total amine content was found to be .00427 mole/gr. and the hydroxyl number

$$31.3=\frac{\text{mg. KOH}}{\text{grams}}$$

EXAMPLE III

0.7 mole (224.7 grams) of aminopropylcocamine (Armour's Duomeen C) were charged to a 500 ml. flask equipped with a thermometer, stirrer and downward condenser to vacuum take-off. The charge was heated at 95°–100° C./25 mm. for ¼ hour to remove low boiling amines and water. The vacuum was then released and 0.7 mole (60.3 grams) of γ-butyrolactone were added in 20 min. at 85°–98° C. and held at 93°–98° C. for 2¼ hours. The total amine content was found to be .00236 mole/gram and the hydroxyl number

$$127=\frac{\text{mg. KOH}}{\text{grams}}$$

The pressure was then reduced to 25 mm. and the temperature raised to 190–220° C. for an additional 4 hours. The dark liquid reaction product was soluble in 65/75 Carnation mineral oil. Its total amine value was .00485 mole/gram and the hydroxyl number was

$$39.9=\frac{\text{mg. KOH}}{\text{grams}}$$

EXAMPLE IV

.55 mole (177 grams) of aminopropylcocoamine (Armour's Duomeen C) was charged to a 500 ml. flask equipped with a thermometer, stirrer and downward condenser to vacuum take-off. The charge was heated at 95°/25 mm. for ½ hour. The vacuum was then released and .55 mole (47.3 grams) of γ-butyrolactone added at 95° C. over a period of ½ hour and then held at 92–96° C. for an additional 3 hours. The pressure was then reduced to 50 mm. and the temperature raised to 180–195° C. and held an additional 6 hours. The final product was a dark fluid paste.

EXAMPLE V

½ mole (170.0 grams) of N-stearylpropylene diamine was charged to a 500 ml. flask equipped with a thermometer, stirrer and downward condenser to vacuum take-off. The charge was heated at 95–100° C. and 60 mm. mercury pressure for ¼ hour. ½ mole (43.0 grams) of γ-butyrolactone was added after releasing the vacuum and the reaction mixture held at 95–100° C. for 2¼ hours. A vacuum of 25 mm. was then applied and the temperature raised to and held at 195–235° C. for 3 hours. The final product was a dark paste soluble in

light mineral oil. The total amine content was found to be .00550 mole/gram and the hydroxyl number

$$40.1=\frac{\text{mg. KOH}}{\text{grams}}$$

EXAMPLE VI

½ mole (200.0 grams) of aminopropyl tallow amine (Armour's Duomeen T) was charged to a 500 ml. flask equipped with a thermometer, stirrer and downward condenser to vacuum take-off. The charge was heated at 95–100° C./60 mm. for ½ hour to remove low boilers. ½ mole (43.0 grams) of γ-butyrolactone was added after releasing the vacuum and the reaction mixture held at 95–100° C. for 2¼ hours. A vacuum of 25 mm. was then applied and the temperature raised to and held at 195–235° C. for 3 hours. The final product was a dark paste soluble in mineral oil. The total amine content was found to be .00430 mole/gram and the hydroxyl number

$$32.1=\frac{\text{mg. KOH}}{\text{grams}}$$

In order to determine the utility of the heat treated reaction products of Examples I to VI inclusive, the following tests were employed:

Test A

OIL WELL CORROSION

This test is described in the Committee T–1K of the National Association of Corrosion Engineers reports, and in brief, is conducted as follows: A 1" square weighed mild steel panel is suspended in the organic phase for 10 seconds of a two phase corrosive environment consisting of 900 grams of oxygen free 5% NaCl brine charged with 500 p.p.m. H_2S, and 100 grams of kerosene in a 1 l. Erlenmeyer flask and then aged for 1 week in the aqueous phase. Weight loss due to corrosion in an inhibited system is expressed as a percentage protection compared to an uninhibited system. The following expression delineates the relationship:

$$P=100-100\frac{Wi}{Wu}$$

where

P=percentage protection.

Wi=difference in weight of the panel before and after the above procedure.

Wu=difference in weight to a blank, i.e. weight loss to a similar panel in an uninhibited system as above described.

It should be noted that when an inhibited system contains 100 p.p.m. of additive, P should be 90% or better in order to define a well inhibited system worthy of further commercial consideration.

Test B

THE BAKER-JONES-ZISMAN STATIC DROP TEST

This test is adequately described in Ind. Eng. Chem. 40, 2338 (1948) and 41, 137 (1949). This test, in brief, was conducted as follows: An indented mild steel test specimen was submerged in the organic solution of inhibitor being tested. This was always a crankcase type lubricating oil with an initial boiling point at 760 mm. of 375° C. and a viscosity of 540 centipoises at 25° C. After ageing for 1 hour at 60° C., one drop of distilled water was placed in the indentation beneath the surface of the solution. The system so prepared was held at 60° C. for 48 hours, and then carefully inspected. Any sign of rust or stain when the water rested against the metal was considered grounds for rejection. If no visible stain or rust was present when viewed in good light, the test was considered passed.

Test C

CHIP TEST

In this test, lathe turnings were allowed to fall into solutions of the inhibitors. The chips were then drained and stored in a humidity cabinet which cycled through 100% relative humidity at 55° C. every 2 hours. The chips were inspected daily and time was counted until 10% of the number of chips exhibited visible signs of rust. The inhibitor was rated on the duration to this point as follows:

<24 hours	No inhibition.
to 24 hours	Slight.
1–3 days	Fair.
3–5 days	Good.
5–7 days	Excellent.

In Test A, 90% is considered good inhibition, in Test B, to pass at 0.5% is considered very good indeed, in Test C, only the very best inhibitors rated excellent.

EXAMPLE VII

For Test A, 100 parts per million of each of the heat treated reaction products of Examples III to VI inclusive, based on the entire liquid system were employed. It is generally considered that inhibitors which afford 90% protection in this test are quite good and worthy of further consideration for commercial development. All of the compounds tried of the above class gave at least this degree of protection. The material from Example IV provided an average of 96% protection. A commercial inhibitor offered for this purpose provided an avarage of 88.2%. The product of Example III gave 95.4%, Example V gave 93.6%, and Example VI gave 94.8%. Other commercial products offered as inhibitors or additives were vastly inferior.

The heat treated reaction products of N-alkylaminopropyl-γ-hydroxybutyramides may be used in injecting into casings directly at the side of the oil production or they may be placed into the oil stream at any other point, the closer to the well the better since the farther the products travel with the oil in the pipeline the longer they will provide protection against corrosion. In this manner, the well casings, pumps, equipment of all types, tanks, pipelines, seagoing tank ships, stills, refining equipment are protected against the deleterious effects of corrosion caused by brines, moisture, petroleum components and hydrosulfuric acid which often occurs with petroleum. In addition, it can be expected, in view of the manner and results of Test A above, that ships, returning under ballast, will continue to enjoy the protection of the inhibitor even when the oil is delivered and the tanks and holds are full of seawater.

EXAMPLE VIII

The heat treated reaction products of Examples I to VI inclusive, were subjected to Test B at 2% and 0.5% concentration. Both of these concentrations passed the test and clearly indicate that the heat treated reaction products are excellent inhibitors.

EXAMPLE IX

The heat treated reaction products of Examples I to VI inclusive, were subjected to Test C. The solvents employed were petroleum ether (at 90–100° C.) and the crankcase lubricant with an initial boiling point at 760 mm. of 375° C. and a viscosity of 650 centipoises at 25° C. The results obtained are as follows:

At 0.5% in the petroleum ether 5% of the chips had visible rust at the end of 1 day and more than 10% at the end of 3 days. At 2% in petroleum ether however, and also at both 0.5% and 2% in the crankcase oil there was not more than 10% rust at the end of 6 days. From this test is was clearly manifest that the inhibition of the heat treated reaction products was excellent when compared with uninhibited solvents which allow rusting to occur in a matter of minutes.

EXAMPLE X

The heat treated products of Examples I to VI inclusive, were subjected to Test C. At the end of the test, the results obtained show that at 2% in the petroleum ether, 10% of the chips did not develop rust until after 4 days, which is considered good; and at 0.5% over 2 days were required to develop rust. In the crankcase lubricant, the products showed excellent results, i.e. no rusting on the chips.

From Examples VII to X inclusive, it is clearly manifest that the solutions of the heat treated reaction products of N-alkylaminopropyl-γ-butyramides are particularly useful for the protection of ferrous metals which are normally exposed to moisture, atmosphere, etc. the inhibitors may be applied as a cutting oil, as a slushing compound, may be brushed on, rubbed on, wiped on, pointed on, dipped, etc. The compounds may be applied to the metal as soon as convenient, and the protection will endure until such time as it may be desired to remove it. The treatment is especially suitable for the treatment and preservation of metal components used in manufacturing, such as gears, crankshafts, metal stamping bodies of automobiles, bicycles, motorcycles, cement mixers, outboard motors, electric hand drills and all other machinery and other things made of ferrous metals.

It is to be noted that the reaction products of N-alkylaminopropyl-γ-hydroxybutyramides, prior to heat treatment, are characterized by the following general formula:

$$R—NHCH_2CH_2CH_2NHCOCH_2CH_2CH_2OH$$

wherein R has the same value as above. Following the heat treatment at 170–250° C. and a pressure below atmospheric, a heat treated product is obtained which differs from the starting material as shown by the difference in the amine and hydroxyl numbers. Although we do not know nor can we ascribe with any degree of accuracy the structure of the treated products, we do know from the observations obtained during the course of our experimentation that the heat treatment of the reaction products of N-alkylaminopropyl-γ-butyramides yields products or compositions that are chemically different from the untreated products. The untreated products gel in hydrocarbon solvents and light mineral oils whereas the corresponding heat treated products do not form gels. We are certain however, that the heat treatment causes a chemical reaction to occur which changes the chemical nature of the starting material. The chemical nature of the heat treated product is not fully known at the present time. It is believed however, that the heat treatment changes the N-alkylaminopropyl-γ-hydroxybutyramide to some other chemical compound. Regardless of the nature or constitution of the heat treated reaction product of N-alkylaminopropyl-γ-hydroxybutyramide, Examples VII to X inclusive, clearly demonstrate that they are unusual as corrosion inhibitors and may be employed as preventatives of corrosion of ferrous metals, as slushing compounds, and the like.

We claim:

1. A composition of matter obtained by heat treating a product consisting of at least one N-alkylaminopropyl-γ-hydroxybutyramide having the following general formula:

$$R—NHCH_2CH_2CH_2NHCOCH_2CH_2CH_2OH$$

wherein R represents an alkyl group of from 8 to 23 carbon atoms at a temperature of 170 to 250° C. and a pressure of 10 to 50 mm. of mercury absolute.

2. A composition of matter obtained according to claim 1 wherein R in the formula of the N-alkylamino propyl-γ-hydroxy butyramide is an octyl group.

3. A composition of matter obtained according to

claim 1 wherein R in the formula of the N-alkylamino propyl-γ-hydroxy butyramide is an octadecyl group.

4. A composition of matter obtained according to claim 1 wherein the product consists of the reaction of 1 mole of γ-butyrolacetone with 1 mole of a mixture of amines having the following composition:

	Percent
Octadecenylamine	35
Octadecylamine	10
Octadecadienylamine	45
Hexadecylamine	10

5. A composition of matter obtained according to claim 1 wherein the product consists of the reaction of 1 mole of γ-butyrolacetone with 1 mole of a mixture of amines having the following composition:

	Percent
Octylamine	8
Decylamine	9
Dodecylamine	47
Myristylamine	18
Hexadecanylamine	8
Octadecylamine	5
Octadecadienylamine	5

6. A composition of matter obtained according to claim 1 wherein the product consists of the reaction of 1 mole of γ-butyrolactone with 1 mole of a mixture of amines having the following composition:

	Percent
Tetradecylamine	2
Hexadecylamine	24
Octadecylamine	28
Octadecenylamine	46

7. The process of preparing a heat treated composition which comprises heating at a temperature of 170 to 250° C. and a pressure of 10 to 50 mm. of mercury absolute a product consisting of at least 1 N-alkylaminopropyl-γ-hydroxybutyramide having the following general formula:

$$R—NHCH_2CH_2CH_2NHCOCH_2CH_2CH_2OH$$

wherein R represents an alkyl group of from 8 to 23 carbon atoms.

8. The process according to claim 7 wherein R in the N-alkylaminopropyl-γ-hydroxybutyramide is an octyl group.

9. The process according to claim 7 wherein R in the N-alkylaminopropyl-γ-hydroxybutyramide is an octadecyl group.

10. The process according to claim 7 wherein the product consists of the reaction of 1 mole of γ-butyrolactone with 1 mole of a mixture of amines having the following composition:

	Percent
Octadecenylamine	35
Octadecylamine	10
Octadecadienylamine	45
Hexadecylamine	10

11. The process according to claim 7 wherein the product consists of the reaction of 1 mole of γ-butyrolactone with 1 mole of a mixture of amines having the following composition:

	Percent
Octylamine	8
Decylamine	9
Dodecylamine	47
Myristylamine	18
Hexadecanylamine	8
Octadecylamine	5
Octadecadienylamine	5

12. The process according to claim 7 wherein the product consists of the reaction of 1 mole of γ-butyrolactone with 1 mole of a mixture of amines having the following composition:

	Percent
Tetradecylamine	2
Hexadecylamine	24
Octadecylamine	28
Octadecenylamine	46

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