

1

3,379,650

DISPERSION OF LONG CHAIN ALKYL AMMONIUM HUMATE IN ORGANIC LIQUID

Augustus Earl Beasley, Jr., Jack C. Cowan, and Hugh G. Gainey, Houston, Tex., assignors to National Lead Company, New York, N.Y., a corporation of New Jersey

No Drawing. Filed Dec. 20, 1963, Ser. No. 332,279

2 Claims. (Cl. 252-308)

This invention relates to dispersion aids for expediting the dispersion of long chain ammonium salts of humic acid in organic liquids.

Humic acid is a material of wide distribution, being present in soils, peat, and coals, especially coals of the type known as lignite or brown coal. Although the exact details of its chemical structure are not completely known, it is a surprisingly uniform substance considering the variety of source materials of which it represents a natural product of degradation, such as leaves, wood, and like vegetable organic matter. It is an acid, in which both carboxyl and phenolic hydroxyl groups contribute base-combining ability. It is soluble in alkalies, such as caustic soda and sodium carbonate, has a deep brown color, and is readily soluble in water when converted to its alkali metal salt, which may be then termed an alkali metal humate, the commonest example of which is sodium humate.

As indicated, it is present in soils and peat, and may readily be extracted from these by known means, most commonly by treatment with dilute aqueous alkali. Whenever it is a matter of producing a commercial humate, that is, whenever economic considerations are of importance, then the humic acid is nearly always derived from its most abundant common source, which is lignite, of which there are vast deposits distributed throughout the world, including the United States, and particularly the states of North Dakota, Texas, New Mexico, and California.

It is possible to make derivatives of humic acid which have the general nature of organic salts thereof in which the cationic portion is an ammonium ion bearing a long hydrocarbon chain. In general, salts of this type are produced by making a salt of humic acid in which the cation is an ammonium ion, containing nitrogen in its pentavalent form and in which there is attached to the nitrogen atom, either directly or indirectly, an alkyl radical having from 12 to 22 carbon atoms in a straight chain. The simplest type of such a long chain ammonium ion is a substituted ammonium ion in which at least one of the hydrogen atoms has been replaced by a long alkyl chain such as has just been described. The remaining hydrogen atoms may remain as such or be substituted by either long alkyl chains of the type just described, or by shorter alkyl chains, having accordingly from 1 to 11 carbon atoms, or even by aryl or alkaryl radicals such as phenyl or benzyl radicals. Thus, there are included in the sub-group just described primary, secondary, tertiary and quaternary amines bearing at least one long chain alkyl radical. Also included in the scope of the term "long chain ammonium ion" are such nitrogen onium ions in which at least one long chain alkyl radical of from 12 to 22 carbon atoms in length is attached to the nitrogen atom through an intermediate linkage, most generally a heterocyclic carbon-nitrogen ring. Included with this second sub-group are such common and commercially available long chain ammonium ions as the alkyl pyridinium and alkyl imidazolium ions. In these latter, the heterocyclic radical contains five members, four of which are carbon in pyridinium, and three of which are carbon in imidazolium, the remainder in both cases being nitrogen. In the imidazolium ion, only one of the nitrogens is capable

2

of pentavalency, and thus it furnishes the onium character to the ion. Further the term "alkyl" is herein used in its broad sense to include alkyl chains containing one or more double bonds, such as for example, oleyl. For convenience, we will term such humates as have just been described "long chain alkyl ammonium humates."

Some examples of humate salts of such long chain alkyl ammonium humates will now be given:

TABLE I

- 10 Dodecylammonium humate
- Stearylammonium humate
- Oleylammonium humate
- Palmitylammonium humate
- 15 Docosylammonium humate
- Methyldodecylammonium humate
- Methylstearylammonium humate
- Di-dodecylammonium humate
- Laurylstearylammonium humate
- 20 Butyldocosylammonium humate
- Benzylaurylammonium humate
- Dimethylaurylammonium humate
- Methylaurylstearylammonium humate
- Tri-laurylammonium humate
- 25 Diphenylstearylammonium humate
- Trimethylaurylammonium humate
- Benzyl-diethyl-docosylammonium humate
- Phenyl-di-butyl-octadecylammonium humate
- Dimethyl-di-octadecylammonium humate
- 30 Benzyl-butyl-lauryl-oleylammonium humate
- Dimethyl-di-(hydrogenated tallow fatty alkyl) ammonium humate
- Methyl-tri-laurylammonium humate
- Methyl-tri-(hydrogenated tallow fatty alkyl) ammonium humate
- 35 1-hydroxyethyl, 2-heptadecenyl, 2-imidazolium humate
- 1-benzyl, 1-hydroxyethyl, 2-heptadecyl-2-imidazolium humate

40 Long chain alkyl ammonium humates of the general type just described are useful in various systems which include an organic liquid vehicle. Thus, for example, they may be used in compounding oil-base drilling fluids, using a liquid medium, e.g., fuel or diesel oil. They are also useful in the manufacture of printing inks, in improving the suspension of pigments in paints, and the like.

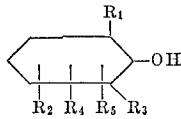
We have found that these long chain alkyl ammonium humates are, as one might expect, more readily dispersible in some organic liquids than in others. Also, the dispersibility of these long chain ammonium humates is dependent to some extent on their processing during manufacture. For example, where the long chain alkyl ammonium humate is prepared by metathesis, precipitating the salt by bringing together aqueous solutions of, say, sodium humate and the selected long chain alkyl ammonium chloride, if the precipitate is flushed directly out of its aqueous reaction bath into the organic liquid with which it is to be incorporated, then its dispersion in the latter is generally much more quickly accomplished than if it is first dried and granulated or ground. Where a given long chain alkyl ammonium humate is difficult to disperse in a given system, the application of heat and agitation, including milling in a colloid mill or the like, will generally achieve the desired degree of dispersion. These measures, however, are inherently time-consuming and add to the total cost of preparation, and it is extremely desirable to be able to produce a long chain alkyl ammonium humate which will disperse in an organic liquid, particularly in a relatively non-polar organic liquid, with a minimum of processing.

70 An object of the present invention is to provide an additive for long chain alkyl ammonium humates of the type

described which facilitates their dispersion in organic liquids.

Other objects of the invention will appear as the description thereof proceeds.

Generally speaking, and in accordance with an illustrative embodiment of our invention, we incorporate with a long chain alkyl ammonium humate which is to be used in an organic liquid vehicle, a chemical compound, or indeed mixtures of several thereof, chosen from the group which consists of the following:



where

R_1 may be C_nH_{2n+1} with n from 1-12;

C_nH_{2n-1} with n from 1-12;

OH, H, Cl, Br, COOH, NH_2

R_2 may be C_nH_{2n+1} with n from 1-12;

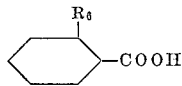
C_nH_{2n-1} with n from 1-12;

H, Cl, Br, phenyl, benzyl

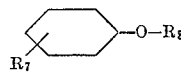
R_3 may be OH, Cl, Br, H, NH_2 , $CONH_2$, phenyl, benzyl;

R_4 may be Cl, Br, H, $HOCH_2-$, methylol;

R_5 may be Cl, Br, H, $HOCH_2-$, methylol;



where R_6 may be H, OH, COOH;



where

R_7 is C_nH_{2n+1} with n between 7 and 11, inclusive; and

R_8 is $(CH_2CH_2O)_mH$ with m between 1 and 18, inclusive;

R_9COOH

where

R_9 may be C_nH_{2n+1} with n between 1 and 13, inclusive;

C_nH_{2n-1} with n between 2 and 15, inclusive;

C_nH_{2n-3} with n between 3 and 17, inclusive;

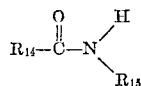
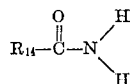
$R_{10}OH$

where R_{10} is C_nH_{2n-1} with n between 1 and 12, inclusive;

$R_{11}R_{12}R_{13}N$

where R_{11} is ethylol, and

R_{12} and R_{13} may be H, ethylol.

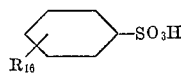


where

R_{14} may be C_nH_{2n+1} with n between 12 and 17, inclusive;

C_nH_{2n-1} with n between 12 and 17, inclusive;

R_{15} is $(CH_2)_mOH$ with m between 1 and 3, inclusive.



where R_{16} is C_nH_{2n-1} with n between 9 and 15, inclusive;

$R_{17}(OCH_2CH_2)_mOH$

where R_{17} is C_nH_{2n+1}

with n between 9 and 15, inclusive,

and m is between 3 and 10, inclusive;

α -naphthol;

β -naphthol;

phenyl acetate;

diphenylamine;

phenyl propionate

maleic acid;

5 malic acid;

glycolic acid;

phthalic acid;

monomethyl ether resorcinol;

monoethyl ether resorcinol

10 piperidine

mono-, di-, tri-oleic ester of sorbitan

mono-, di-, tri-lauric ester of sorbitan

2,6-dimethylol, 4-nonyl phenol

octyl resorcinol

15 nonyl resorcinol

In order to demonstrate the effectiveness of our dispersants, we prepared a long chain alkyl ammonium humate from North Dakota lignite, the method of preparation being one which does not favor a highly readily dispersible reaction product: and we then tested it for dispersibility in fuel oil containing the dispersant to be evaluated, again under conditions which did not favor ready dispersion by mechanical means alone. These test conditions actually correspond to plant and field conditions of favorable economy. That is to say, the method of preparation of the long chain alkyl ammonium humate was, as will be seen hereinbelow, accomplished without prior dissolution of the lignite to free the humic acid and without the use of a highly alkaline solution with a long time being taken for such dissolution; moreover; the humic acids were not physically separated from the remainder of the lignite, as might be done in a more complicated and necessarily more expensive method of preparation. Finally the long chain alkyl ammonium humate was dried and ground before testing. Such products are inherently more readily dispersible before such drying and grinding but this again entails the shipment of liquid or moist concentrates as distinguished from a dry product and thus requires the use of steel drums instead of bags, and thus likewise would increase the manufacturing and shipping costs. Finally, in dispersing the long chain alkyl ammonium humate in diesel oil to determine its dispersibility, only a 5-minute stir was used. This again corresponds to conditions which often obtain for example, in an oil field where immediate results are desired from the incorporation of an additive in a drilling fluid, and where such additive would therefore be less valuable if it required, say, 24 hours of circulation in the well before dispersing to exhibit its full effect. All of these conditions will become clear in the light of the test procedure which will now be given.

Two hundred grams of naturally weathered North Dakota lignite were combined with 2 liters of water and 72 grams borax. This was stirred for 45 minutes at 170° F. Then 200 grams of commercial di(hydrogenated tallow alkyl) dimethylammonium chloride were melted and added to the mixture just described. The corresponding long chain alkyl ammonium humate (with the dross) separated out in a flocculant state, the mother liquor being clear. The entire batch was stirred for 15 minutes and filtered, the solid product then being dried for 16 hours at 160° F. and finally ground to pass a 60 mesh screen.

This inherently rather slowly dispersible long chain alkyl ammonium humate preparation was tested by mixing 65 15 grams thereof with 350 ml. of diesel oil and 5 grams of the dispersing additive to be tested. This mixture was stirred 5 minutes on a laboratory mixer of the "Waring Blendor" type. The resulting slurry was then tested for filter loss by the method standardized by the American Petroleum Institute in which the mixture is pressure-filtered through hardened filter paper of 3-inch diameter at 100 lbs. per square inch for 30 minutes. The filtrate, which consisted of the diesel oil carrying any of the humates in solution which had dispersed or dissolved there- 75 in finely enough to pass a hardened filter paper, was

tested in a photoelectric colorimeter by the following procedure: one part of the filtrate was diluted with 14 parts of diesel oil and the light absorption measured on the colorimeter which was standardized at zero for diesel oil, and in which complete non-transmission of light gave 100 on the scale. The volume of the filtrate in milliliters obtained in the 30-minute test was recorded as the API filtrate.

In view of the conditions chosen for the experiment, which hindered the ready dispersibility of the otherwise untreated long chain alkyl ammonium humate, the API filtrate for the case of a non-dispersing additive was over 50 ml. (shown as "50-"); and the color of the diluted filtrate gave a reading of less than 25 on the colorimeter. This may be compared with the first entry in the table which follows, from which it may be seen that phenol gave an API filter loss of 1.0 and a color of 90 (as already stated, the color of the starting diesel oil without any humate was 0, and its API filter loss was about 50 to 100 ml.).

Table II below gives the results obtained for a large number of dispersing additives within the purview of our invention. Table III gives the results for a large number of additives which are not within the purview of our invention.

TABLE II

Dispersing Additive	API*	Color
Phenol.....	1.0	90
o-Benzyl phenol.....	1.3	76
Octyl resorcinol.....	1.8	79
Catechol.....	1.0	60
Pyrogallol.....	2.0	88
Pentachloro phenol.....	0.8	60
2-bromo, 4-phenyl phenol.....	1.0	85
2-amino, 4-chloro phenol.....	1.0	95
2,6-dichloro phenol.....	1.8	61
"Penta" phenol (amyl phenol).....	1.0	90
Octyl phenol.....	1.6	90
Nonyl phenol (bottoms).....	1.2	90
Nonyl phenol.....	1.8	90
Dodecyl phenol.....	1.8	90
Salicylamide.....	6.2	80
Salicylic acid.....	0.6	94
Mono-ethyl ether resorcinol.....	1.5	85
Di-nonyl-phenol.....	9.0	Dark
Benzoic acid.....	1.5	84
Phthalic acid.....	1.0	85
Dodecyl benzene sulfonic acid.....	1.8	70
α -Naphthol.....	0.8	Dark
β -Naphthol.....	1.2	Dark
Phenyl acetate.....	1.8	71
Phenyl propionate.....	1.0	70
2, 6-dimethylol, 4-nonyl phenol.....	0.5	Dark
Diphenylamine.....	2.0	76
Nonyl phenol condensed with ethylene oxide:		
1 mole EtO.....	2.8	Dark
4 moles EtO.....	2.2	Dark
9.5 moles EtO.....	2.6	Dark
12 moles EtO.....	4.4	Dark
Formic acid.....	1.3	88
Acetic acid.....	2.2	90
Butyric acid.....	4.1	84
Hexanoic acid.....	1.6	83
Octanoic acid.....	6.3	78
Decanoic acid.....	3.4	75
Dodecanoic acid.....	1.7	64
Myristic acid.....	4.4	66
Oleic acid.....	2.5	67
Linoleic acid.....	2.2	80
Acrylic acid.....	1.8	89
Maleic acid.....	1.0	90
Malic acid.....	2.6	60
Glycolic acid.....	0.8	85
Methanol.....	5.4	80
Ethanol.....	9.6	73
n-Propanol.....	12.2	60
n-Butanol.....	7.8	56
n-Amyl alcohol.....	7.5	93
n-Hexyl alcohol.....	6.0	50
n-Octyl alcohol.....	3.7	50
2-ethyl hexyl alcohol.....	5.8	63
Lauryl alcohol.....	3.0	92
Ethanol amine.....	0.5	-----
Diethanol amine.....	1.7	-----
Triethanol amine.....	1.3	-----
Ethoxylated lauryl alcohol:		
1 mol EtO.....	1.8	32
5 mols EtO.....	0.4	50
10 mols EtO.....	0.7	75
15 mols EtO.....	3.8	77
20 mols EtO.....	3.1	75
Sorbitan trioleate +20 moles EtO.....	1.3	72
Sorbitan monolaurate.....	1.2	76
Sorbitan monooleate.....	1.3	78
Sorbitan trioleate.....	1.8	68
Piperidine.....	5	65

*American Petroleum Institute filter loss in ml.

TABLE III

Additive	API	Color
Cyclohexanol.....	50+	Clear
Hydroquinone.....	50+	Clear
Resorcinol.....	50+	Clear
2,3,4-tetrahydroxy naphthalene.....	75	16
Pyrogallol.....	50	Clear
Sodium pentachlorophenate.....	50	Clear
Para hydroxy benzoic acid.....	50+	Clear
Potassium acid phthalate.....	30	16
Methylphthalate.....	36	24
Nitrobenzene.....	63	22
Sulfanilic acid.....	102	15
Nitro aniline.....	50+	14
1-amino, 2-naphthol sulfonic acid.....	50+	18
Toluene sulfonic acid.....	69	50
Dichloro toluene.....	54	Clear
Chloro benzene.....	50+	Clear
Benzaldehyde.....	37	38
Toluene.....	50+	Clear
Dodecyl chlorobenzene.....	59	Clear
Palmitic acid.....	50+	0
Stearic acid.....	9	0
Succinic acid.....	50+	-----
Succinic anhydride.....	50+	-----
Fumaric acid.....	50+	Clear
Myristyl alcohol.....	50+	Clear
Cetyl alcohol.....	3.5	Clear
Stearyl alcohol.....	8.4	Clear
Di-aldehyde starch.....	41	22
Sorbitol.....	50+	17
Amylamine.....	84	Light
n-Hexylamine.....	84	Light
Octylamine.....	68	Light
2 ethyl hexylamine.....	66	Light
Sec laurylamine.....	68	Light
Tri capryl amine.....	70	Light
Di-isopropanol amine.....	144	Light
Pinacolone.....	30	17
Glycine.....	76	13
Propionitrile.....	32	53
Propionamide.....	75	-----
Hyd. tallow amide.....	24	25
Formamide.....	75	-----
Chloroethene.....	121	11
Dodecyl bromide.....	46	18
Straight chain alkanes.....	50+	Clear
Benzene.....	50+	Clear
Carbon tetrachloride.....	117	Clear
p-Xylene.....	50+	Clear
Naphthalene.....	50+	Clear
Methylene blue.....	54	35
Furfural.....	47	46
Quinoline.....	45	-----
Thiophene.....	23	14
Pyridine.....	44	22

As a further example of our invention, and at the same time a further example of a method of making long chain alkyl ammonium humate, the following experimental results are given:

45 A long chain amine humate was made by reacting a primary long chain amine in the free base form with lignite in the acid form. The latter was made by adding 3 kilograms of North Dakota naturally weathered lignite with 7 liters of concentrated sulphuric acid, which served not only to acidify the humic acid present in the lignite but also to remove calcium ion. After standing 3 hours at room temperature, the mixture was diluted with distilled water so that the acidified lignite flocculated out. The latter was filtered and washed until free of excess acid, and then dried overnight at 150° F.

In order to prepare the long chain alkyl ammonium humate, 1 liter of water was heated and maintained at 160° F. to 180° F., and 40 grams of primary hydrogenated tallow alkyl amine (which was largely normal octadecyl amine) and 100 grams of the acid lignite just described were added. Flocculation occurred promptly, and the product was recovered by filtration, dried at 150° F. overnight, and then tested as follows:

65 Samples of (a) 350 ml. of diesel and (b) 350 ml. of diesel oil with 10 grams of the long chain alkyl ammonium humate just described dispersed therein by stirring for 2 minutes, were both tested by the American Petroleum Institute pressure filtration test already described. In the case of both (a) and (b), no shut-off was obtained and all of the fluid emerged as filtrate. The test was repeated with (c) 315 ml. diesel oil with 35 ml. normal octyl alcohol which had 10 grams of the same long chain alkyl ammonium humate described hereinabove, dispersed therein by stirring for 2 minutes. In the case of (c), the API filtration test gave a 30 minute

fluid loss of 7 ml. Thus, the only difference between (b) and (c) was that in the latter, the fluid vehicle contained approximately 10% by volume of normal octyl alcohol, and this sufficed to disperse the long chain alkyl ammonium humate with the minimal stirring of 2 minutes so that it gave a very low fluid loss.

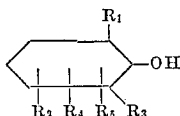
The relative proportions of the dispersing additive to the long chain alkyl ammonium humate may vary over a considerable range. The ratios which we find usable in practice vary from 1:100 to 1:1, this being the weight ratio of the dispersing additive to the humate. The particular choice of a ratio within this range will depend on working conditions, such as the degree of mechanical agitation available to aid in the dispersion of the long chain alkyl ammonium humate in the organic vehicle; it will vary to some extent with the organic vehicle itself; it will vary with the temperature of the system during dispersion; it will vary with the fineness of grind of the humate; it will vary with the drying conditions under which the humate was made; and like factors which will be apparent to chemical engineers and those skilled in the art generally. However, the range of ratios just given corresponds to the practical, usable range.

The organic vehicle in which the long chain alkyl ammonium humate is dispersed, with the aid of the dispersing additive, again may be highly variable in its nature, depending upon the end use of the system concerned. Thus, for example, where drilling fluids and fracturing fluids for use in the working of oil wells are concerned, the organic vehicle will generally be a petroleum oil, such as kerosene, diesel fuel, fuel oil, light lubricating oil, and the like. Where molding sands are involved, the organic vehicle may again be a petroleum oil. Where printing inks are involved, again the organic vehicle may be petroleum oil, or it may be more in the nature of a lacquer formulation in which the organic vehicle is a volatile solvent or solvent mixture. Since the long chain alkyl ammonium humates are useful in many systems in which an organic vehicle is incorporated, it will be apparent that the choice of particular organic vehicles is equally broad.

It will be apparent that while we have described our invention with the aid of numerous specific examples, and have disclosed exemplary proportions, quantities, procedures, and the like, our invention is a broad one, and numerous variations in detail, such as choice of ingredients, proportions, processing conditions, and the like may be made without departing from the spirit and scope of the invention, as delineated by the claims which follow.

Having described the invention, we claim:

1. A composition of matter consisting essentially of an organic liquid vehicle chosen from the class consisting of petroleum oils and lacquer solvents, and containing a long chain alkyl ammonium humate and an effective dispersing amount of a substance chosen from the class consisting of:



where

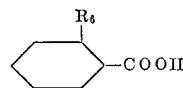
R₁ is chosen from the group consisting of C_nH_{2n+1} with *n* from 1-12; C_nH_{2n-1} with *n* from 1-12; OH, H, Cl, Br, COOH, NH₂

R₂ is chosen from the group consisting of C_nH_{2n+1} with *n* from 1-12; C_nH_{2n-1} with *n* from 1-12; H, Cl, Br, phenyl, benzyl

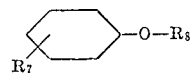
R₃ is chosen from the group consisting of OH, Cl, Br, H, NH₂, CONH₂, phenyl, benzyl;

R₄ is chosen from the group consisting of Cl, Br, H, HOCH₂-, methylol;

R₅ is chosen from the group consisting of Cl, Br, H, HOCH₂-, methylol;



where R₆ is chosen from the group consisting of H, OH, COOH;



where

R₇ is C_nH_{2n+1} with *n* between 7 and 11, inclusive; and R₈ is (CH₂CH₂O)_mH with *m* between 1 and 18, inclusive;

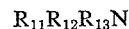


where

R₉ is chosen from the group consisting of C_nH_{2n+1} with *n* between 1 and 13, inclusive; C_nH_{2n-1} with *n* between 2 and 15, inclusive; C_nH_{2n-3} with *n* between 3 and 17, inclusive;

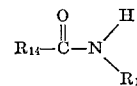
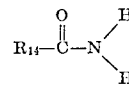


where R₁₀ is C_nH_{2n-1} with *n* between 1 and 12, inclusive;



where R₁₁ is ethylol, and

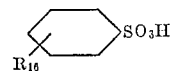
R₁₂ and R₁₃ are chosen from the group consisting of H, ethylol.



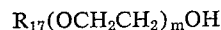
where

R₁₄ is chosen from the group consisting of C_nH_{2n+1} with *n* between 12 and 17, inclusive; C_nH_{2n-1} with *n* between 12 and 17, inclusive;

R₁₅ is (CH₂)_mOH with *m* between 1 and 3, inclusive.



where R₁₆ is C_nH_{2n-1} with *n* between 9 and 15, inclusive;



where R₁₇ is C_nH_{2n+1}

with *n* between 9 and 15, inclusive, and *m* is between 3 and 10, inclusive;

α-naphthol;

β-naphthol;

phenyl acetate;

diphenylamine;

phenyl propionate

maleic acid;

malic acid;

glycolic acid;

phthalic acid;

monomethyl ether resorcinol;

monoethyl ether resorcinol

piperidine

mono-, di-, tri-oleic ester of sorbitan

mono-, di-, tri-lauric ester of sorbitan

2,6-dimethylol, 4-nonyl phenol
 octyl resorcinol
 nonyl resorcinol

2. The composition in accordance with claim 1 in
 which said substance is present in a weight ratio to said
 humate within a range of 1:100 and 1:1. 5

References Cited

UNITED STATES PATENTS

3,190,919	6/1965	Swanson	-----	260—567.6	10
3,168,475	2/1965	Jordan et al.	-----	252—8.5	

OTHER REFERENCES

"Metallic Soaps," Metasap Chemical Co., Harrison,
 N.J., 1940, pages 15-16.

Zimmerman et al.: Supplement I to the 1953 Edition
 of Handbook of Material Trade Names, Industrial Re-
 search Service Inc., Dover, N.H., 1956, page 221.

MURRAY KATZ, *Primary Examiner.*

LEON D. ROSDOL, ALBERT T. MEYERS,
Examiners.

R. D. LOVERING, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,379,650 Dated April 23, 1968

Inventor(s) Augustus Earl Beasley, Jr., et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8. line 25, for "R₁₀" read --R₁₀OH--.

**SIGNED AND
SEALED
JUN 27 1968**

(SEAL)

Attest:

**Edward M. Fletcher, Jr.
Attesting Officer**

**WILLIAM E. SCHUYLER, JR.
Commissioner of Patents**