United States Patent Office

3,322,567

Patented May 30, 1967

3,322,567

METHOD FOR IMPARTING ANTISTATIC PROPERTIES TO ELECTRICALLY NON-CONDUCTIVE SUBSTANCE AND THE RESULTING PRODUCT

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No Drawing. Original application Jan. 16, 1962, Ser. No. 166,699, now Patent No. 3,133,072, dated May 12, 1964. Divided and this application Apr. 3, 1964, Ser. No. 357,257

2 Claims. (Cl. 117—121)

This application is a divisional application of our copending application Ser. No. 166,699, filed Jan. 16, 1962, now issued as Patent No. 3,133,072, dated May 12, 1964.

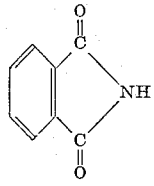
This invention relates to quaternary ammonium compounds, and it particularly relates to anti-static quaternary ammonium cyclic imides.

It has heretofore been found that the reaction products of various quaternary ammonium compounds and benzosulfimide (saccharin) were quite active biocidal agents, generally superior to ordinary quaternary ammonium compounds in this respect and, furthermore, possessed of a sweet, pleasant taste not found in ordinary quaternaries. In addition, it was found that such quaternary ammonium benzosulfimides had inherent antistatic properties when incorporated in electrically non-conductive materials such as paper, glass, rubber, textiles, plastics and the like, and were also capable of being readily complexed with halogens to retain all the highly effective germicidal properties of the halogens while substantially eliminating their undesirable properties such as their relatively high degree of toxicity, their tendency to irritate the skin and their tendency to stain both skin and fabrics. It has also been found that certain quaternary ammonium benzosulfimides have thixotropic properties making them highly desirable thickening agents for various purposes. However, all these properties were heretofore believed limited to the quaternary ammonium benzosulfimides.

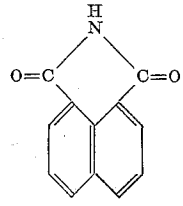
It has now been discovered that the above properties are not limited to the quaternary ammonium benzosulfimide, but are, in addition, possessed in general by all other quaternary ammonium aromatic cyclic imides where the aromatic nucleus has attached thereto in those positions not attached to the cyclic imide radical a member of the group consisting of hydrogen, halogen, alkyl and alkoxy, and wherein the cyclic imide radical has the formula NHCOX wherein X is a member of the group consisting of CO, O, S and N.

Illustrative of the aromatic cyclic imides utilizable in the present invention in addition to benzosulfimide are:

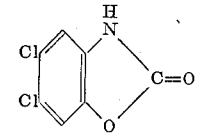
Phthalimide



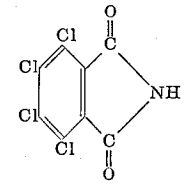
Naphthalimide



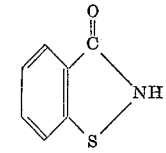
2,6-dichlorobenzoaxolinone



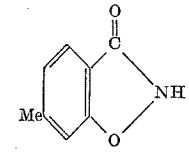
Tetrachlorophthalimide



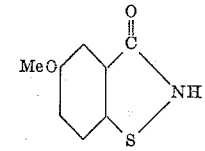
Benzothiazolinone



6-methylbenzoxazolinone



5-methoxybenzothiazolinone



For most purposes, the quaternary ammonium radical may be selected from any of the well-known class of quaternary ammonium groups as, for example, the alkyl quaternaries such as lauryl trimethyl ammonium, stearyl trimethyl ammonium, stearyl dimethyl ethyl ammonium, cetyl dimethyl ethyl ammonium, myristyl dimethyl ethyl ammonium, lauryl dimethyl ethyl ammonium, tallow trimethyl ammonium, hydrogenated tallow trimethyl ammonium, coco trimethyl ammonium, di-hydrogenated tallow dimethyl ammonium, di-coco dimethyl ammonium, di-soya dimethyl ammonium, hydrogenated tallow dimethyl ethyl ammonium, coco dimethyl ethyl ammonium, tallow dimethyl ethyl ammonium and soya dimethyl ethyl ammonium; the alkylaryl quaternaries such as lauryl dimethyl benzyl ammonium, alkyl dimethyl benzyl ammonium, cetyl dimethyl benzyl ammonium, stearyl dimethyl benzyl ammonium, alkyl dimethyl dichlorobenzyl ammonium, alkyl dimethyl ethyl benzyl ammonium, alkyl dimethyl dimethyl benzyl ammonium, dodecyl benzyl trimethyl ammonium, dodecyl methyl benzyl trimethyl ammonium, octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium, soya dimethyl benzyl ammonium, hydrogenated tallow dimethyl benzyl ammonium, tallow dimethyl benzyl ammonium and coco dimethyl benzyl ammonium; the alkyl and alkylaryl pyridiniums; the alkyl and alkylaryl isoquinoliniums such as alkyl isoquinolinium, cetyl isoquinolinium and dodecyl benzyl isoquinolinium; the alkyl and alkylaryl picoliniums such as alkyl alpha picolinium, alkyl beta picolinium and alkyl gamma picolinium; the imidazoliniums such as alkenyl benzyl hydroxyethyl imidazolinium, alkenyl dichlorobenzyl hydroxyethyl imidazolinium, alkenyl ethyl benzyl hydroxyethyl imidazo-

linium, alkenyl dichlorobenzyl hydroxyethyl imidazolinium, coco benzyl hydroxyethyl imidazolinium, coco ethyl hydroxyethyl imidazolinium, stearyl ethyl hydroxyethyl imidazolinium, stearyl benzyl hydroxyethyl imidazolinium, stearyl dichlorobenzyl hydroxyethyl imidazolinium and stearyl ethyl benzyl hydroxyethyl imidazolinium; the morpholiniums such as coco methyl morpholinium and myristil methyl morpholinium; and the N-pyridiniums such as N-(stearoyl colamino formyl methyl)-pyridinium and N-(lauroyl colamino formyl methyl)-pyridinium.

The quaternary ammonium aromatic cyclic imides of the above type are, as stated, generally all effective in the manner disclosed except that only particular ones are thixotropic and, therefore, suitable as thickening agents. These thixotropic compounds are those wherein the quaternary radical comprises four alkyl groups attached to the nitrogen atom, one of these groups being a long chain group having at least 14 carbon atoms in the chain, preferably 14–22 carbon atoms, and the other three groups being lower alkyls having no more than 5 carbon atoms in the chain. Among the quaternaries within this scope are myristyl trimethyl ammonium, cetyl trimethyl ammonium, stearyl trimethyl ammonium, arachidyl trimethyl ammonium, behenyl trimethyl ammonium, myristyl dimethyl ethyl ammonium, cetyl dimethyl ethyl ammonium, stearyl dimethyl ethyl ammonium, arachidyl dimethyl ethyl ammonium, behenyl dimethyl ethyl ammonium, and the like.

The various compounds embodying the present invention are generally prepared in substantially the same manner by reacting stoichiometric amounts of a selected quaternary ammonium salt, such as a halide or sulfate, with a selected aromatic cyclic imide or with an alkali metal salt of such imide in an aqueous solution wherein the components react with each other to form the desired product. Alternatively, an alcoholic solution may be used instead of the aqueous solution. Usually, agitation is required and the reaction may be carried out at ambient temperatures although, generally, the application of additional heat is preferable.

The following specific examples are provided for illustrative purposes only and with no intent to necessarily limit the inventive scope except as claimed:

Example 1

319.5 gms. of "Arquad 16–50" (produced by the Armour Chemical Division, Armour & Co., Chicago, Ill.), a product containing a 50% by weight concentration of cetyl trimethyl ammonium chloride, were diluted with 320 grams of deionized water, thereby making a 25% solution of the chloride. 92.5 grams (½ mol) of potassium phthalimide were dissolved in 277 grams of deionized water. The two solutions were then blended and agitated for 5 minutes at ambient temperature and pressure to form a clear aqueous solution. This solution was then evaporated to dryness in a forced draft oven at 212° F. The dry residue was extracted with hot 99% methanol. The alcoholic solution was then agitated and filtered and the insoluble salt removed. The filtrate was then evaporated to dryness. The residue was cetyl trimethyl ammonium phthalimide.

Example 2

380 grams of a 50% aqueous solution of alkyl dimethyl benzyl ammonium chloride were diluted to 25% solids with 380 grams of deionized water. 98.5 grams (½ mol) of naphthalimide were dissolved in 10 liters of deionized water containing 20 grams of sodium hydroxide. The two aqueous solutions were then mixed and heated, with agitation, to 100° C. An oily layer formed on the surface and was separated in a separatory funnel. This oily layer was then dried in a vacuum oven at 140° F. to produce alkyl dimethyl benzyl ammonium naphthalimide as the end product.

Example 3

187.8 grams (½ mol) of cetyl pyridinium chloride were dissolved in 1 liter of 99% ispropanol. 102 grams (½ mol) of 2,6-dichlorobenzoxazolinone were dissolved in 1 liter of 99% isopropanol. The two alcoholic solutions were then mixed together with agitation and during the agitation 20 grams of sodium hydroxide dissolved in 400 grams of ethyl alcohol were added to the mixture. The resulting solution was evaporated to 1 liter and cooled to room temperature, after which the salt sodium chloride was removed. The filtrate was then further evaporated to dryness. The residue, a dark brown, pasty solid, was cetyl pyridinium 2,6-dichlorobenzoxazolinone.

Example 4

224.5 grams (½ mol) of octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride were dissolved in 1 liter of deionized water. 161.5 grams of potassium tetrachlorophthalimide were dissolved in 5 liters of deionized water. The two aqueous solutions were then mixed and heated to 212° F. An oily layer was obtained and this oily layer was separated in a separatory funnel and then dried in a vacuum oven. The resultant residue was octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium tetrachlorophthalimide.

Example 5

68.5 grams (½ mol) of benzothiozolinone were dissolved in 1 liter of isopropanol. 359 grams of a 50% solution of dodecyl benzyl trimethyl ammonium chloride were added with agitation. 20 grams of sodium hydroxide dissolved in 400 grams of ethyl alcohol were then added with agitation. The resultant solution was then evaporated to dryness in vacuum oven at 140° F. The resultant residue was then dissolved in 1 liter of 99% isopropanol. The resultant salt precipitated out and was removed by filtration. The filtrate was then evaporated to dryness in a vacuum oven at 140° F. The final product obtained was a brown, pasty solid identified as dodecyl benzyl trimethyl ammonium benzothiozolinone.

Example 6

233 grams (½ mol) of lauryl isoquinolinium bromide at 75% strength was diluted to 25% strength with 466 grams of isopropanol. 99.5 grams of 6-methyl phthalimide was dissolved in 298 grams of deionized water. The alcoholic quaternary solution and the water solution of the phthalimide were then mixed and heated to 212° F. The non-aqueous layer, a brown, viscous mass, was then separated and dried in a vacuum oven. The resultant brown, pasty solid was identified as lauryl isoquinolinium 6-methyl phthalimide.

Example 7

83.5 grams (½ mol) of 5-methoxy benzothiozolinone were dissolved in 1 liter of isopropanol. 192.75 grams (½ mol) of cetyl dimethyl benzyl ammonium chloride were dissolved in 1 liter of deionized water. The alcoholic benzothiozolinone solution and the aqueous quaternary solution were then mixed and to the mixture was added 20 grams of sodium hydroxide. The resultant solution was evacuated to dryness in a vacuum oven at 140° F. and the solute was taken up with 1 liter of isopropanol. The resultant salt precipitated out and was removed by filtration. The filtrate was then dried in a vacuum oven at 140° F. The residue constituting the final product was a yellow powder identified as cetyl dimethyl benzyl ammonium 5-methoxy benzothiozolinone.

Example 8

192.75 grams of cetyl dimethyl benzyl ammonium chloride (½ mol) were diluted to 10% solids with deionized water and this solution was then heated to 160° F. at which point 28.5 grams of iodine crystals were added with agitation until the iodine was completely dissolved. The 10% quaternary ammonium iodine complex was then

cooled to 75° F. 87.5 grams (½ mol) of potassium phthalimide was dissolved in deionized water to make a 10% aqueous solution and this latter solution was then added to the quaternary solution with rapid and vigorous agitation. The resultant complex was separated as a crystalline mass and the supernatent water solution was decanted. The precipitate was then further washed with deionized water. The cetyl dimethyl benzyl ammonium phthalimide-iodine complex was then filtered and dried under reduced pressure.

Illustrative of the biocidal properties of the compounds of the present invention, bacteriostatic tests involving the following minimum concentrations of representative compounds gave halos of at least 1 mm. in agar plate studies:

Compound	*Staphylococcus aureus* 209, percent	E. Coli, percent	E typhosi, percent	*Staph. aur.* Antibiotic-resistant str., percent
Alkyl dimethyl benzyl ammonium benzosulfimide	0.01	0.1	0.1	0.01
Alkyl dimethyl benzyl ammonium phthalimide	0.01	0.1	0.1	0.01
Alkyl dimethyl benzyl ammonium naphthalimide	0.01	0.1	0.1	0.01
Alkyl dimethyl benzyl ammonium 2,6-dichlorobenzoxazolinone	0.01	0.1	0.1	0.01
Alkyl dimethyl benzyl ammonium tetrachlorophthalimide	0.01	0.1	0.1	0.01
Alkyl dimethyl benzyl ammonium benzothiozolinone	0.01	0.1	0.1	0.01
Alkyl dimethyl benzyl ammonium phthalimide-bromine (10% bromine)	0.006	----------	0.06	0.006

The above compounds within the scope of the present invention having quaternary radicals comprising four alkyl groups attached to the nitrogen atom, wherein one alkyl group is a long chain of at least 14 carbon atoms and the other three are lower alkyls of 1 to 5 carbon atoms, have very effective thixotropic properties. These properties are retained and may even be enhanced in the presence of alkali metal, ammonium or alkaline earth salts. For example, such compounds have been shown to retain their thixotropic properties in aqueous solutions of 10% sodium chloride, 10% calcium chloride and 5% sodium sulfate.

The following example of a white, indoor, water-base paint illustrates the thixotropic properties of the above type compound:

Component:	Parts by wt.
Behenyl trimethyl ammonium phthalimide (1.5% solution in H_2O)	100
"Tamol–731" (a sodium salt of a condensed aryl sulfonic acid; produced by Rohm & Haas Co., Philadelphia, Pa.) in 25% aqueous solution	5
"Colloid–606" (produced by Colloids, Inc., Newark, N.J.)	3
Ethylene glycol	20
"Titanox RA–50" (titanium dioxide pigment; produced by Titanium Pigment Corp., div. of Nat'l Lead Co., New York, N.Y.)	220
"Snowflake" (a diatomaceous earth produced by Johns-Manville Corp., New York, N.Y.)	75
"Celite 231" (a diatomaceous earth produced by Johns-Manville Corp., New York, N.Y.)	50
Carbitol	16
"Igepol CO–630" (100% nonyl phenoxy polyoxyethylene ethanol produced by General Aniline and Film Corp., New York, N.Y.)	3
Water	250
Polyvinyl acetate (water emulsion having 50% solids)	345
"A.S.P.–400" (a clay produced by Minerals & Chemicals Corp. of America, Metuchen, N.J.)	75

The behenyl trimethyl ammonium phthalimide, the "Tamol–731," the "Colloid 606," the ethylene glycol, the "Titanox RA–50," the "Snowflake," the "A.S.P.–400" and the "Celite–281" are mixed until a smooth paste is formed. The water is then added to achieve the desired milling viscosity and the mass is passed through a suitable milling machine. The carbitol, "Igepol CO–630" and polyvinyl acetate are then added and thoroughly mixed into the composition. If necessary, additional water may be added to adjust the viscosity as desired.

The thixotropic properties of the above type compounds make them ideal thickening agents not only for paints but for lotions, creams and the like. They are also effectively used in the drilling of oil since they act to keep the clay in suspension and prevent its settling out, thereby keeping the clay fluid and preventing clogging. They also are effective thickeners for pumping mixtures which are used to carry up the drilling refuse and simultaneously act as biocides against algae and the like, thereby reducing the slime. They also act to automatically seal up leaks and fissures in the substrata.

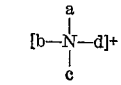
Quaternary ammonium aromatic cyclic imides of the type contemplated herein are also very effective antistatic agents when physically combined with electrically non-conductive substances such as paper, textiles, skins, leathers, furs, plastics, etc. They may be incorporated in waxes and polishes for furniture, automobiles, floors, walls and the like. These waxes and polishes, when applied to the surfaces to be treated, prevent the accumulation of dust, dirt, grime, etc. which would otherwise occur as the result of static electricity on such surfaces. Furthermore, these compounds are substantive to all of the aforementioned materials while their compatibility with polymeric substances such as epoxy resins, phenolics, acrylate, cellulose ester, polyolefins, polyurethanes, polyvinyls, nylon, etc. make them ideal for blending, impregnating or coating such materials.

The terminology "physically combining" and "physical combination" is used herein to designate blending, impregnating or coating as distinguished from "chemically combining" wherein there is a chemical reaction between the substances.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

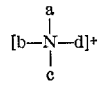
The invention claimed is:

1. A method of providing antistatic properties in electrically non-conductive substances that are normally subject to the accumulation of static electricity which comprises physically combining with said electrically non-conductive substance an antistatically effective amount of a quaternary ammonium aromatic cyclic imide wherein the quarternary ammonium cation has the formula:



wherein *a* and *b* are members of the group consisting of alkyl and cyclic constituents of pyridinium, isoquinolinium, picolinium, imidazolinium and morpholinium, *c* is a member of the group consisting of alkyl, alkylaryl, aryl and cyclic constituents of pyridinium, isoquinolinium and picolinium, *c*, when it is a cyclic constituent, being a member of the same ring as *a* and *b*, and *d* is a member of the group consisting of alkyl and alkylaryl, and wherein the aromatic cyclic imide anion is a member of the group consisting of phthalimide, naphthalimide, benzoxazoninone and benzothiazolinone, the aromatic portion of said anion being substituted by a member of the group consisting of hydrogen, halide, lower alkyl and lower alkoxy, there being a direct electro-valent linkage between the quaternary ammonium cation and the aromatic cyclic imide anion.

2. An electrically non-conductive shaped body that is normally subject to the accumulation of static electricity, said body having antistatic properties and comprising a physical combination of said electrically non-conductive substance and an antistatically effective amount of a quaternary ammonium aromatic cyclic imide wherein the quaternary ammonium cation has the formula:



wherein *a* and *b* are members of the group consisting of alkyl and cyclic constituents of pyridinium, isoquinolinium, picolinium, imidazolinium and morpholinium, *c* is a member of the group consisting of alkyl, alkylaryl, aryl and cyclic constituents of pyridinium, isoquinolinium and picolinium, *c*, when it is a cyclic constituent, being a member of the same ring as *a* and *b*, and *d* is a member of the group consisting of alkyl and alkylaryl, and wherein the aromatic cyclic imide anion is a member of the group consisting of phthalimide, naphthalimide, benzoxazolinone and benzothiazolinone, the aromatic portion of said anion being substituted by a member of the group consisting of hydrogen, halide, lower alkyl and lower alkoxy, there being a direct electro-valent linkage between the quaternary ammonium cation and the aromatic cyclic imide anion.

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