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POLYMETHYLENE-BIS-BENZOTHIAZOLIUM SALTS

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1 Claim. (Cl. 260—304)

This invention relates to polymethylene-bis-benzothiazolium salts and a method for making them.

A number of quaternary salts containing heterocyclic nuclei are useful in supersensitizing photographic silver halide emulsions. See, for example, Carroll et al. U. S. Patent 2,334,864, issued November 23, 1943. The bis-compounds, or "double-enders," are particularly useful for this purpose because of their tendency to be non-wandering. Allen et al. U. S. Patent 2,500,110, issued March 7, 1950, describes bis-pyridyl quaternary salts which can be used to advantage to supersensitize photographic silver halide emulsions optically sensitized with a sensitizing dye.

We have now found new bis-benzothiazolium salts which can advantageously be used as antifoggants for photographic silver halide emulsions, rather than as supersensitizers for photographic silver halide emulsions.

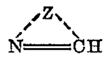
It is, therefore, an object of our invention to provide polymethylene-bis-benzothiazolium salts. Another object is to provide a method for making such quaternary salts. Other objects will become apparent from a consideration of the following description and examples.

Polymethylene-bis-benzothiazolium quaternary salts containing a reactive group, such as methyl, in the 2-position have been previously described in Wilson U. S. Patent 2,425,774, issued August 19, 1947. The quaternary salts of Wilson are useful as intermediates in the preparation of polymeric cyanine dyes, although they are not particularly efficacious as antifoggants. The quaternary salts of the instant invention are especially useful as antifoggants for photographic silver halide emulsions.

According to our invention, we provide new polymethylene-bis-benzothiazolium salts by a process which comprises heating together a benzothiazole base with an alkylene halide.

Typical benzothiazole bases include those represented by the following general formula:

I



$$N\overset{Z}{=\!=}CH$$

wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series. Especially useful is benzothiazole itself, and benzothiazoles containing a substituent on the benzene ring of the benzothiazole nucleus, such as alkyl, aryl, alkoxyl, halogen, hydroxyl, etc. Typical are benzothiazole, 6-methoxybenzothiazole, 6-ethoxybenzothiazole, 5-phenylbenzothiazole, 6-phenylbenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 5-hydroxybenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-ethylbenzothiazole, etc.

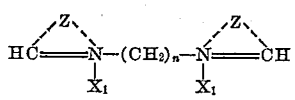
Typical alkylene halides include those represented by the following general formula:

II $$X_1-(CH_2)_n-X_1$$

wherein X_1 represents a halogen atom, such as chlorine, bromine, etc. and *n* represents a positive integer of from 1 to 9. Particularly useful are the alkylene bromides.

The temperature used can be varied, depending on the particular reactants. In general, temperatures of from about 5° C. to 150° C. can be used. In general, about two molecular equivalents of the benzothiazole base (Formula I) are employed to each molecular equivalent of the alkylene halide (Formula II). The polymethylene-bis-benzothiazolium salts thus produced can be represented by the following general formula:

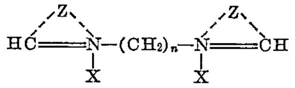
III



$$HC\overset{Z}{=\!=}\underset{X_1}{N}-(CH_2)_n-\underset{X_1}{N}\overset{Z}{=\!=}CH$$

wherein Z, X_1, and *n* have the values set forth above. The halide anion (X_1 above) can be replaced by other anions by usual double decomposition procedures. It is thus possible to produce polymethylene-bis-benzothiazolium salts of the following general formula:

IV

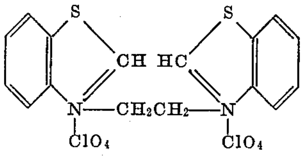


$$HC\overset{Z}{=\!=}\underset{X}{N}-(CH_2)_n-\underset{X}{N}\overset{Z}{=\!=}CH$$

wherein Z and *n* have the values set forth above, and X represents an anion, such as chloride, bromide, iodide, perchlorate, sulfamate, ethylsulfate, p-toluenesulfonate, benzenesulfonate, acetate, thiocyanate, etc.

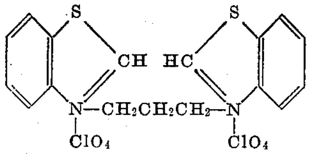
The following examples will serve to illustrate more fully the manner whereby we practice our invention.

Example 1.—Ethylene-bis-benzothiazolium perchlorate



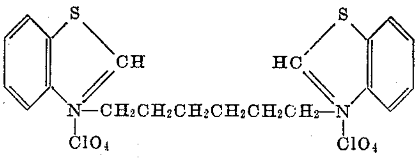
A mixture of 5.4 parts of benzothiazole and 3.8 parts of ethylene bromide was heated for 20 hours at 120–125° C. On cooling, the mixture set to a "glass" that was broken up by treatment with hot methanol. In this way 3 parts of an orange colored solid was obtained, which was essentially ethylene-bis-benzothiazolium bromide. The material dissolved in water to give a deep red solution which was decolorized to yellow with a decolorizing carbon (Nuchar). By treatment of an aqueous solution of this bromide with an aqueous solution of sodium perchlorate, ethylene-bis-benzothiazolium perchlorate was formed as a pale yellow crystalline solid.

Example 2.—Trimethylene-bis-benzothiazolium perchlorate



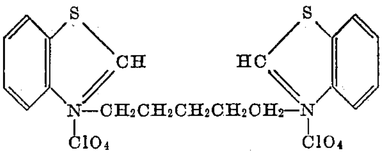
A mixture of 10.1 parts of trimethylene bromide and 13.5 parts of benzothiazole was heated for 3 hours at 120°–125° C. The resulting product was dissolved in water, and the solution was filtered to remove a small amount of insoluble material. The filtrate was decolorized with decolorizing carbon, filtered from the decolorizing carbon, and treated with an excess of sodium perchlorate. On cooling to room temperature, 10.5 parts of trimethylene-bis-benzothiazolium perchlorate separated.

Example 3.—Hexamethylene-bis-benzothiazolium perchlorate



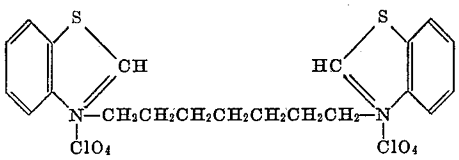
In a procedure similar to Example 2, 9 parts of hexamethylene bromide and 10 parts of benzothiazole heated together for four hours at 120–130° C. gave 15 parts of hexamethylene-bis-benzothiazolium perchlorate (after treatment with $NaClO_4$).

Example 4.—Pentamethylene-bis-benzothiazolium perchlorate



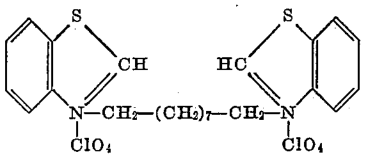
A mixture of 2.7 parts of benzothiazole and 2.3 parts of pentamethylene bromide was heated for 3 hours at 135° C. The "glassy" solid resulting on cooling was dissolved in 40–50 cc. of methanol. The warm methanol solution of the reaction product, which was essentially pentamethylene-bis-benzothiazolium bromide, was treated with a solution of 5 parts of sodium perchlorate in 8 parts of warm water. Pentamethylene-bis-benzothiazolium perchlorate (3 parts) separated immediately as a yellowish granular product. The material had only slight solubility in water and alcohol. It was recrystallized from a large volume of methanol. It formed pale yellow needles melting at about 208° C.

Example 5.—Heptamethylene-bis-benzothiazolium perchlorate



Heptamethylene bromide (5.2 parts) and benzothiazole (5.4 parts) were mixed and heated for 15 hours at 130° C. with stirring. The resulting product was worked up as set forth in Example 2, 10 parts of sodium perchlorate being used to form the heptamethylene-bis-benzothiazolium perchlorate. The crude product (7.5 parts) was recrystallized from methanol to give a material that melted at 178–180° C.

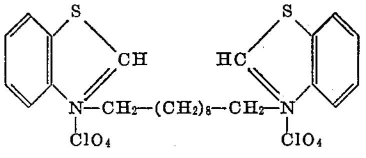
Example 6.—Nonamethylene-bis-benzothiazolium perchlorate



This material was prepared from nonamethylene bromide and benzothiazole by exactly the same procedure described in Example 5. In this manner, 5.7 parts of nonamethylene bromide and 5.4 parts of benzothiazole gave 8 parts of crude nonamethylene-bis-benzothiazolium perchlorate. Recrystallization of the crude from methanol gave a material melting at 193–195° C.

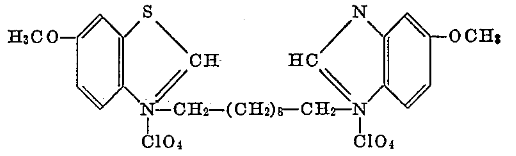
Other bis-benzothiazolium salts which can be obtained according to our invention include the following:

Example 7.—Decamethylene-bis-benzothiazolium perchlorate



A mixture of 10 parts of decamethylene bromide and 9 parts of benzothiazole was heated at 120–130° C. for two hours. The reaction mixture was dissolved in about 100 parts of methanol. The hot methanolic solution was treated with a decolorizing carbon and filtered. To the filtrate was added an excess of an aqueous solution of sodium perchlorate. There was immediate precipitation of a yellow solid which is essentially decamethylene-bis-benzothiazolium perchlorate. The yield was 12.5 parts.

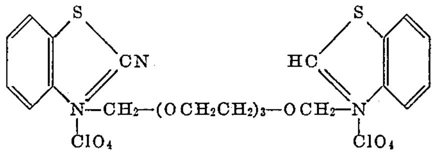
Example 8.—Decamethylene-bis-6-methoxybenzothiazolium perchlorate



This salt was prepared in a manner similar to that described in Example 7 above.

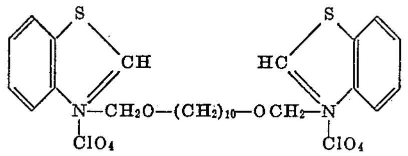
Although the above examples describe our invention with particular reference to bis-benzothiazolium salts wherein the intercyclic chain is composed of methylene $(-CH_2)$ groups, it is to be understood that our invention also comprises similar compounds wherein the polymethylene chain is interrupted with one or more oxygen or sulfur atoms. The following examples illustrate methods for preparing such bis-benzothiazolium salts.

Example 9.—Ethylene-bis (oxyethoxymethylbenzothiazolium perchlorate)



Ethylene-bis (oxyethoxymethyl chloride) (3.7 parts) in dry benzene (5 parts) was added dropwise to a solution of benzothiazole (4.4 parts) in benzene. The reaction was carried out at 5–15° C. The produce separated in "tacky" form. It was taken up in cold water; the aqueous layer was separated from the benzene layer and washed with ether. This aqueous solution was added to an excess of sodium perchlorate in water. Ethylene-bis-(oxyethoxymethylbenzothiazolium perchlorate) separated as an oil from which the aqueous layer was decanted. The oil was washed with cold water and after standing became solid. The solid was stirred with ether and then collected on a filter. The yield was 2.1 parts. The melting point was 78–93° C. It was recrystallized from a mixture of methanol and acetone by the addition of ether. The product thus obtained melted at 134–135° C.

Example 10. — Decamethylene-bis-oxymethylbenzothiazolium perchlorate

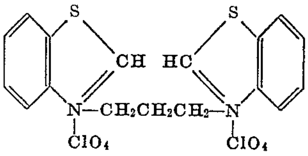


To a solution of 8.8 parts of benzothiazole in 35 parts of dry benzene was added (dropwise) 81. parts of decamethylene-bis-oxymethyl chloride in 10 parts of benzene. The gelatinous material that separated was dissolved by the addition of 50 parts of cold water. The aqueous layer was separated from the benzene layer and washed with ether to remove any unchanged starting materials. The aqueous solution of decamethylene-bis-(oxymethylbenzothiazolium chloride) was added to an excess of sodium perchlorate in 10 parts of water. An oily precipitate which solidified on standing was formed. It was collected on a filter, washed with cold water and then with acetone. In this manner 4.7 parts of crude decamethylene-bis-oxymethylbenzothiazolium perchlorate, melting at 125–133° C. was obtained. It was recrystallized from methanol. By such treatment it separated in long white needles, melting at 130–132° C.

In lieu of using bases of Formula I above wherein Z represents the non-metallic atoms to complete a heterocyclic nucleus of the benzothiazole series, we have prepared bis-quaternary salts using bases of Formula I above wherein Z represented the non-metallic atoms necessary to complete a different nucleus, such as benzimidazole, quinoxaline, 2-methylimidazoline, acridine, and cinnoline, however, the bis-quaternary salts thus produced do not provide the advantages which are realized when using the bis-benzothiazolium salts of our invention. The instant bis-benzothiazolium salts are also useful as adjuvants to mixed-grain photographic silver halide emulsions as described in the copending application of Burt H. Carroll, S. N. 251,833, filed on even date herewith (now U. S. Patent 2,673,149, issued March 23, 1954).

What we claim as our invention and desire secured by Letters Patent of the United States is:

The compound represented by the following formula:



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2,515,913	Zandt et al.	July 18, 1950

FOREIGN PATENTS

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