Patented Mar. 7, 1950 2,500,110

UNITED STATES PATENT OFFICE

2,500,110

BISPYRIDYL COMPOUNDS CONTAINING A SILICON ATOM AND PROCESS OF PREPARATION

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No Drawing. Application June 12, 1948, Serial No. 32,734

12 Claims. (Cl. 260—290)

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This invention relates to new organic compounds useful as supersensitizers for photographic silver halide emulsions. More particularly, this invention relates to bis-(pyridyl)-alkoxysilanes and to a process for their preparation.

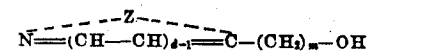
It is known that the inherent sensitivity of photographic silver halide emulsions (whether spectrally sensitized or not) can be increased, and there has been a constant effort to produce higher and higher speeds in photographic emulsions.

We have now found that the quaternary ammonium salts of bis-(pyridyl)-alkoxysilanes, i. e., compounds in which the linkage between carbon and silicon is interrupted by oxygen, sensitize photographic silver halide emulsions (whether spectrally sensitized or not) and have the added advantage of not diffusing appreciably from the emulsions into the film support upon which the emulsions are usually coated.

It is, accordingly, an object of our invention to provide a new class of chemical compounds and a process for preparing them. Another object of our invention is to provide a new class of chemical compounds which are useful in increasing the speed and sensitivity of photographic silver halide emulsions. Still another object is to provide a new class of chemical compounds useful in increasing the speed and sensitivity of photographic silver halide emulsions which do not diffuse from the emulsions into the film support upon which the emulsions are usually coated. A still further object is to provide photographic silver halide emulsions (whether spectrally sensitized or not) sensitized with a new class of chemical compounds, and to a process for preparing such emulsions. Other objects will become apparent from a consideration of the following description.

According to the process of our invention, we prepare our new compounds by interacting an alcohol containing as a substituent, a heterocyclic nucleus of the pyridine series, and an organic dihalosilane. The process is advantageously carried out in the presence of a tertiary organic amine.

The alcohols containing, as a substituent, a heterocyclic nucleus of the pyridine series, which are useful in practicing our invention, can advantageously be represented by the general formula:

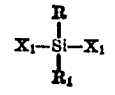


wherein Z represents the non-metallic atoms

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necessary to complete a heterocyclic nucleus of the pyridine series, *d* represents a positive integer from 1 to 2, and *m* represents a positive integer from 2 to 3. Typical alcohols include, for example, β-(2-pyridyl)-ethanol, γ-(2-pyridyl)-propanol, β-(4-methylpyridyl-2)-ethanol, β-(6-methylpyridyl-2)-ethanol, β-(5-ethylpyridyl-2)-ethanol, β-(4-pyridyl)-ethanol, γ-(4-pyridyl)-propanol, β-(3-ethyl pyridyl-4)-ethanol, etc. In addition to containing alkyl substituents such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, etc. (i. e., an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4), the pyridine nucleus can have substituted thereon such groups as Cl—, Br—, Ch_3O—, C_2H_5O—, C_3H_7O—, etc.

The organic dihalosilanes useful in practicing our invention can advantageously be represented by the general formula:



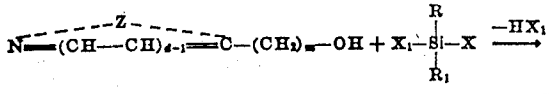
wherein R and R_1 each represents a member selected from the group consisting of an alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, etc. (i. e., an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4) and a mononuclear aryl group of the benzene series, e. g., phenyl (C_6H_5—), o-, m- and p-tolyl ($CH_3C_6H_4$—), o-, m- and p-chlorophenyl (ClC_6H_4—), o-, m- and p-bromophenyl (BrC_6H_4—), etc. and X_1 represents a halogen atom, such as a chlorine atom or a bromine atom. Typical silanes include, for example, dibromodimethylsilane, dichlorodimethylsilane, dichlorodiethylsilane, dichlorodi-n-propylsilane, dichlorodiphenylsilane, dibromodiphenylsilane, di-(p-bromophenyl)-dichlorosilane, dichlorodi-(p-tolyl)-silane, dichloroethylpropylsilane, dichloroethylisobutylsilane, dichloroethylphenylsilane, dichloro-p-bromophenylphenylsilane, etc.

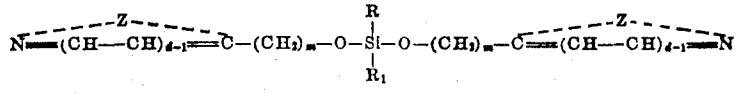
The process of our invention can advantageously be carried out in the presence of an organic amine, such as a tertiary organic amine. Typical tertiary organic amines include, for example, the trialkyl amines, such as triethyl amine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, the tertiary aromatic amines, such as N,N-dimethylaniline, N,N-diethylaniline, N,N-dipropylaniline, etc., and the tertiary heterocyclic amines, such as pyridine, quinoline, isoquinoline, α-picoline, β-picoline, γ-picoline, quinaldine, etc.

The process of our invention can conveniently

be carried out in a solvent which does not react with any of the materials present in the reaction mixture. Typical solvents include the dialkyl ethers, such as diethyl ether, diisopropyl ether, etc., the halogenated hydrocarbons, such as chloroform, carbon tetrachloride, ethylene dichloride, etc., 1,4-dioxane, the normally liquid hydrocarbons, such as n-heptane, benzene, toluene, o-, m- and p-xylenes, etc. The temperature at which our process can be carried out varies and is generally a function of the reactants employed. We have found that temperatures of from 15 to 40° C. are usually sufficient for the purposes of our invention, although lower or higher temperatures can be used, if desired.

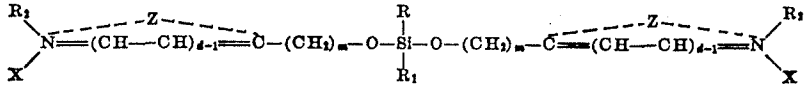
The process of our invention can conveniently be illustrated by the following general equation:





wherein R, R_1, Z, *d* and *m* have definitions designated above. The hydrogen halide HX_1 which is formed during the reaction readily combines with the tertiary organic amine to form a salt which can be filtered off from the reaction mixture.

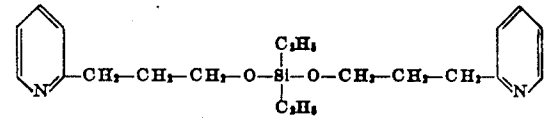
Our new bis-pyridyl compounds, which are obtained as free bases in the reaction illustrated above, can be further treated to obtain their quaternary salts. For example, when the free base is heated with an alkyl ester of p-toluenesulfonic acid, a quaternary ammonium compound is readily formed. Other quaternary ammonium compounds can be readily prepared by heating the free bases with a compound containing an acidic anion. Another method for preparing quaternary ammonium compounds of our new bases comprises heating one of the alkyl sulfuric or sulfonic acid ester addition salts of our new bases with an inorganic salt (i. e., by double decomposition). The quaternary addition compounds which are readily obtainable from our new bases can be represented by the general formula:



wherein R, R_1, Z, *d* and *m* have the definitions designated above, and R_2 represents an alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-n-butyl, amyl, etc. (i. e., an alkyl group of the formula C_nH_{2n+1} wherein *n* represents a positive integer from 1 to 5), and X represents an anion (or acid radical), such as halide (e. g., Cl^-, Br^-, I^-), perchlorate (ClO_4^-), thiocyano (SCN^-), alkylsulfate (e. g., $CH_3SO_4^-$), benzenesulfonate ($C_6H_5SO_2O^-$), p-toluenesulfonate ($p\text{-}CH_3C_6H_4SO_2O^-$), etc. Typical esters which can be reacted directly by heating with our new bases to give useful quaternary salts include dimethylsulfate, diethylsulfate, methylbenzenesulfonate, ethyl benzenesulfonate, n-propyl benzenesulfonate, methyl p-toluenesulfonate, ethyl p-toluenesulfonate, n-propyl p-toluenesulfonate, n-butyl p-toluenesulfonate, isobutyl p-toluenesulfonate, sec-n-butyl p-toluenesulfonate, n-amyl p-toluenesulfonate, etc. Compounds wherein X in the above formula represents a bromide ion or an iodide ion can conveniently be prepared by interacting a quaternary salt of our bis-pyridyl compounds, such as the d-methyl-p-toluenesulfonate, with potassium bromide and potassium iodide, respectively. Compounds where X represents a perchlorate (ClO_4^-) ion can advantageously be prepared by interacting a quaternary salt of our bis-pyridyl compounds, such as the dimetho-p-toluenesulfonate, with sodium perchlorate. Compounds where X represents a chloride ion or a thiocyano (SCN^-) ion can conveniently be obtained by interacting a quaternary salt where X represents an iodide ion with a methanol suspension of silver chloride or silver thiocyanate, respectively. Other methods of preparing our new quaternary ammonium compounds can be used, if desired. Such methods are commonly employed and are well known to those skilled in the art. For example, compounds where X represents a halide ion can be prepared by heating our new free bases with the appropriate alkyl halide in a sealed tube.

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

Example I.—Diethyl-di-[γ-(2-pyridyl)-propoxy] silane

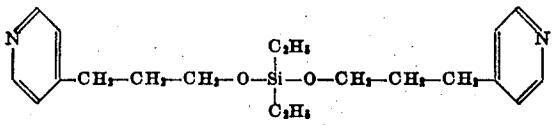


35.1 parts by weight of γ-(2-pyridyl)-propanol (B. P. 134 to 139° C./11 mm.) were dissolved in 250 parts by weight of anhydrous diethyl ether, and 30 parts by weight of triethylamine added. While this solution was vigorously stirred, a second solution of 20 parts by weight of redistilled technical dichlorodiethylsilane in anhydrous diethyl ether was added dropwise. After the addition was complete, the mixture was stirred for an additional hour at room temperature (20–25° C.) and then filtered. The ethereal filtrate was washed thoroughly with water, dried, and after removal of the ether, the residue was fractionally distilled under a vacuum. There were thus obtained 33 parts by weight of diethyl-di-[γ-(2-pyridyl)-propoxy] silane distilling at 194 to 198° C./1.5 mm. The analysis of this compound was as follows:

	Calculated	Found
C	67.0	67.2
H	8.4	8.3
N	7.8	7.9

When an ethereal solution of 0.256 mol of γ-(4-pyridyl)-propanol was reacted with an ethereal solution of 0.127 mol of dichlorodiethyl-

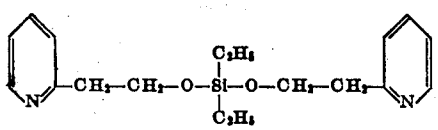
silane in the presence of triethylamine in exactly the same manner as described in Example I, diethyl-di-[γ-(4-pyridyl)-propoxy] silane boiling at 210 to 216° C./1.5 mm. was obtained. The formula of this compound can be represented as:



The analysis of this compound was as follows:

	Calculated	Found
C	67.0	66.5
H	8.4	7.9
N	7.8	8.1

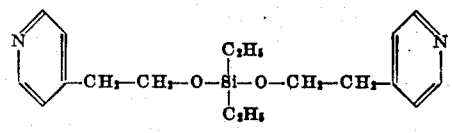
Example II.—Diethyl-di-[β-(2-pyridyl)-ethoxy] silane



31.5 parts by weight of β-(2-pyridyl)-ethanol were dissolved in 250 parts by weight of anhydrous ether, and 30 parts by weight of triethylamine added. While vigorously stirring this solution, a second solution of 20 parts by weight of redistilled technical dichlorodiethylsilane in anhydrous diethyl ether was added dropwise. After the addition was complete, the mixture was stirred for an additional hour at room temperature (20 to 25° C.) and then filtered. The ethereal filtrate was washed thoroughly with water, dried and, after distilling off the ether from the solution, the residue was fractionally distilled. There were thus obtained 28.6 parts by weight of diethyl-di-[β-(2-pyridyl)-ethoxy] silane as a pale yellow liquid distilling at 158 to 162° C./1 mm. The analysis of this compound gave the following results:

	Calculated	Found
C	65.4	64.9
H	7.9	7.8

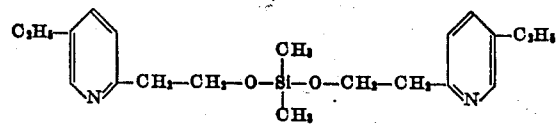
When an ethereal solution of 0.256 mol of β-(4-pyridyl)-ethanol was reacted with an ethereal solution of 0.127 mol of dichlorodiethylsilane in the presence of triethylamine in exactly the same manner as described in Example II, diethyl-di-[β-(4-pyridyl)-ethoxy] silane distilling at 199 to 204° C./3mm. was obtained. The formula of this compound can be represented as:



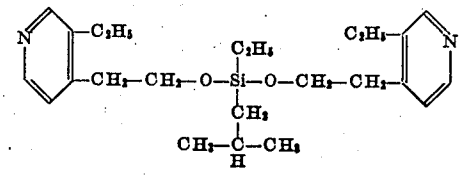
The analysis of this compound gave the following results:

	Calculated	Found
C	65.4	64.8
H	7.9	7.8

When an ethereal solution of 0.256 mol of β-(5-ethylpyridyl-2)-ethanol is reacted with an ethereal solution of 0.127 mol of dibromodimethylsilane in the presence of quinoline in exactly the same manner as described in Example II, di-[β-(5-ethylpyridyl-2-ethoxy] dimethylsilane represented by the formula:

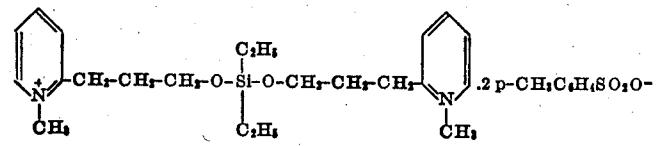


can be obtained. In like manner, when an ethereal solution of 0.256 mol of β-(3-ethylpyridyl-4)-ethanol is reacted with an ethereal solution of 0.127 mol of dichloroethylisobutylsilane in the presence of dimethylaniline, di-[β-(3-ethylpyridyl-4)-ethoxy] ethylisobutylsilane represented by the formula:



can be obtained.

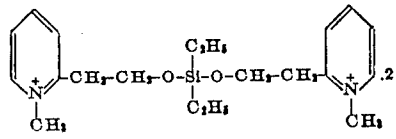
Example III.—Diethyl - di - [γ -(2 - pyridyl)-propoxy] silane dimetho-p-toluenesulfonate



4.8 parts by weight of methyl p-toluenesulfonate were added to 3.6 parts by weight of the diethyl-di-[γ-(2-pyridyl)-propoxy] silane obtained in Example I, and the mixture was heated at 100 to 105° C. on an oil bath for one hour. The excess methyl p-toluenesulfonate which was used was removed by extraction with warm benzene, all traces of which were removed under reduced pressure. A quantitative yield (7.3 parts by weight) of diethyl-di-[γ-(2-pyridyl)-propoxy] silane dimetho-p-toluenesulfonate was obtained. It was found to be soluble in water, ethyl alcohol or hot acetone, but insoluble in hydrocarbon solvents, such as benzene, etc.

When 4.8 parts by weight of methyl p-toluenesulfonate were added to 3.6 parts by weight of the diethyl-di-[γ-(4-pyridyl)-propoxy] silane obtained in Example I, diethyl-di-[γ-(4-pyridyl)-propoxy] silane dimetho-p-toluenesulfonate, which exhibited solubility properties similar to those of the product obtained in Example III, was obtained. When either of these dimetho-p-toluenesulfonates are warmed with a methanol solution of potassium iodide, the corresponding dimeth iodides are readily formed. When these dimeth iodides are warmed with a methanol solution of silver thiocyanate (Ag SCN), the corresponding dimetho thiocyanates are formed with ease.

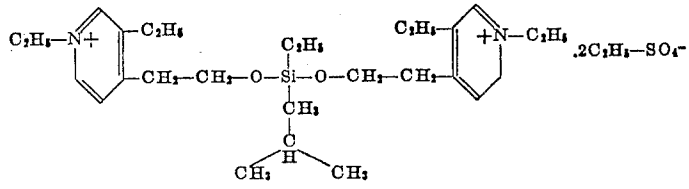
Example IV.—Diethyl-di-[β-(2-pyridyl) ethoxy] silane dimetho-p-toluenesulfonate



4.8 parts by weight of methyl p-toluenesulfonate were added to 3.3 parts by weight of the diethyl-di-[β-(2-pyridyl)-ethoxy] silane obtained in Example II, and the mixture was heated on a steam bath for one hour. The excess methyl p-toluenesulfonate which was used was removed by extraction with warm benzene, all traces of which were removed by warming the residue under a vacuum. An almost quantitative yield (6.5 parts by weight) of diethyl-di-[β-(2-pyridyl)-ethoxy] silane dimetho p-toluenesulfonate was thus obtained. It was found to be soluble in water, ethyl alcohol or warm acetone, but insoluble in hydrocarbon solvents, such as benzene.

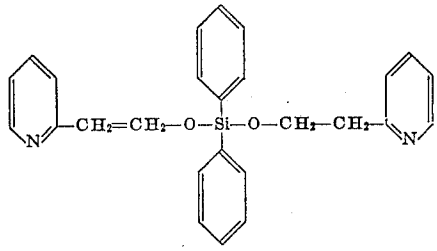
When 4.8 parts by weight of methyl p-toluenesulfonate were added to 3.3 parts by weight of diethyl-di-[β-(4-pyridyl)-ethoxy] silane obtained in Example II, and the mixture warmed on a steam bath for one hour, diethyl-di-[β-(4-pyridyl)-ethoxy] silane dimetho p-toluenesulfonate, which exhibited solubility properties similar to those of the products obtained in Examples III and IV, was obtained. When either of these dimetho p-toluenesulfonates are warmed with a methanol solution of sodium perchlorate, the corresponding dimetho perchlorates are readily formed.

Similarly, when 0.01 mol of di-[β-(3-ethylpyridyl-4)-ethoxy] ethylisobutylsilane is warmed with 0.0275 mol of diethylsulfate, and the excess diethylsulfate removed as described above, di-[β-(3-ethylpyridyl-4)-ethoxy] ethylisobutylsilane diethyl sulfate represented by the formula:



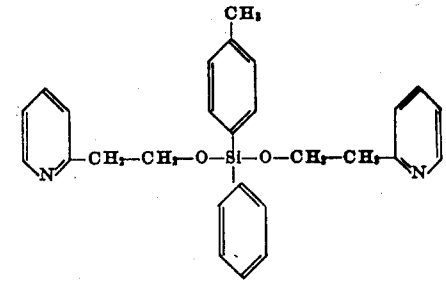
can be obtained.

Example V.—Diphenyl-di-[β-(2-pyridyl-ethoxy] silane



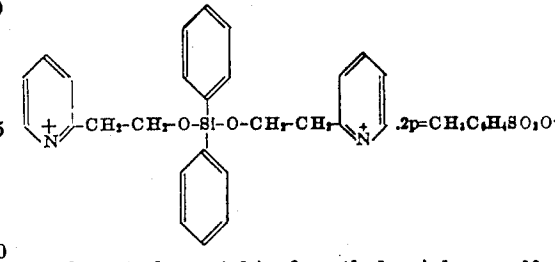
31.5 parts by weight of β-(2-pyridyl)-ethanol were dissolved in 250 parts by weight of anhydrous diethyl ether, and 30 parts by weight of triethylamine added. While this solution was vigorously stirred, a second solution of 32.1 parts by weight of redistilled technical dichlorodiphenylsilane in anhydrous diethyl ether was added dropwise. After the addition was complete, the mixture was stirred for an additional hour at room temperature (20–25° C.) and then filtered. The ethereal filtrate was washed thoroughly with water, dried, and after removal of the ether, the residue was fractionally distilled under a vacuum. There was thus obtained, diphenyl-di-[β-(2-pyridyl)-ethoxy] silane as a yellow oil distilling at 221° C./1 mm. This oil darkened on standing.

When a molecularly equivalent amount of dichlorodi-(p-tolyl) silane is reacted with β-(2-pyridyl)-ethanol in accordance with the process described above, di-[β-(2-pyridyl)-ethoxy] di-(p-tolyl) silane represented by the formula:



is formed.

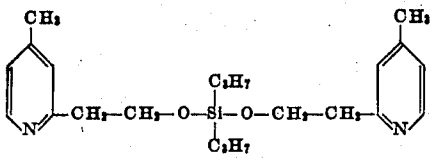
Example VI.—Diphenyl-di-[β-(2-pyridyl)-ethoxy] silane dimetho-p-toluenesulfonate



4.8 parts by weight of methyl p-toluenesulfonate were added to 4.3 parts by weight of the diphenyl-di-[β-(2-pyridyl)-ethoxy] silane obtained in Example V, and the mixture was heated on a steam bath at 100–110° C. for one hour. The excess methyl p-toluenesulfonate was removed by dissolving the reaction mixture in water and extracting with benzene. The last traces of methyl p-toluenesulfonate were removed by warming the aqueous solution in a vacuum, and the water was then removed under reduced pressure. There remained an almost quantitative yield of diphenyl-di-[β-(2-pyridyl)-ethoxy] silane dimetho-p-toluenesulfonate as an amber oil. It was soluble in water, alcohol, and acetone, but insoluble in benzene. When this dimetho-p-toluenesulfonate is reacted with a methanol solution of potassium bromide, the quaternary salt, diphenyl-di-[β-(2-pyridyl)-ethoxy] silane dimethobromide is readily formed. Similarly, by reacting this dimetho-p-toluenesulfonate with a methanol solution of potassium iodide, diphenyl-di-[β-(2-pyridyl)-ethoxy] silane dimethiodide is formed.

Operating in a similar manner, other bis-

pyridyl compounds, as well as their quaternary ammonium salts, can be prepared by reacting alkanols substituted by a pyridyl nucleus with other organic dihalogenosilanes in the presence of a tertiary organic amine. For example, when β-(4-methylpyridyl-2)-ethanol is reacted with dichlorodipropylsilane in the presence of triethylamine, di-[β-(4-methylpyridyl-2)-ethoxy] dipropylsilane represented by the formula:



can be obtained. When propyl benzenesulfonate is warmed with this base, the dipropo benzenesulfonate addition salt is readily formed.

In accordance with our invention, the polyammonium salts of our bis-pyridyl compounds can be incorporated in photographic silver halide emulsions in any suitable form, e. g., in the form of a solution in a suitable solvent, such as water or methyl alcohol. The polyammonium salts should be thoroughly incorporated in the emulsion. Since the introduction of halide anions into photographic silver halide emulsions alters the halide concentration in the emulsion, and compensating changes in the emulsion may be desirable, if such poly-ammonium salts are employed, we generally prefer to employ polyammonium salts containing anions other than halides. Perchlorates and p-toluenesulfonates have been found to be especially useful.

In the case of spectrally sensitized emulsions, the polyammonium salts of our bis-pyridyl compounds can be incorporated in the emulsion before, simultaneously with or after the sensitizing dye, although in some cases it may be advantageous to incorporate the sensitizing dye before incorporating the polyammonium salt. The methods of incorporating sensitizing dyes in emulsions are, of course, well known to those skilled in the art. Ordinarily, it is advantageous to employ a solution of the sensitizing dye in a suitable solvent, e. g., methyl alcohol; ethyl alcohol or acetone can be employed in cases where the solubility of the sensitizing dye in methyl alcohol is very low. Sensitizing dyes are ordinarily incorporated in the washed, finished emulsions, and, in accordance with our invention, the polyammonium salts are advantageously also incorporated in the washed, finished emulsions. However, the polyammonium salts can be added to the emulsion during the preparation thereof, i. e., during the precipitation, the first digestion or the second digestion (ripening). After preparing the emulsions in the presence of the polyammonium salts, the sensitizing dyes can be incorporated in the so-prepared emulsions.

The quantity of the polyammonium salt which is most advantageously employed varies with the nature of the polyammonium salt and with the nature of the emulsion. In most instances, a satisfactory concentration was found to be between about 20 mg. and 200 mg. of the polyammonium salt per gram-mole of silver halide in the emulsion, although greater or smaller concentrations could be employed. We have found, however, that too large quantities of the polyammonium salts are advantageously avoided, since excesses tend to produce fog in the emulsions.

The upper range of concentration for any particular one of our polyammonium salts in any particular type of emulsion can be determined by employing a series of concentrations of the polyammonium salt separately in several batches of the same emulsion, and determining the sensitivity of the several emulsions before and after incorporation of our polyammonium salt or salts. This method of determining the optimum concentration may be carried out in any conventional manner. Briefly, the method we would employ would comprise coating the aforementioned emulsions in suitable thickness onto glass plates and then testing the resultant photographic plates in a wedge spectograph and a sensitometer, whereby the spectral sensitivity and speed of the emulsion on the plate may be determined.

When employing spectrally sensitized emulsions, the spectral sensitizers are advantageously employed in about their optimum concentration, which, for most purposes may be considered as lying between about 3 mg. and 20 mg. of spectral sensitizer per liter of emulsion containing about 0.25 mole of silver halide, although it is to be understood that these values are merely set forth for purposes of illustration and the concentrations above or below the aforementioned concentrations can be employed. With fine-grain emulsions (which includes many of the ordinarily employed silver chloride emulsions), the ratio of the sensitizing dye to the concentration of the silver halide in the emulsion may advantageously be larger than in the coarser-grained emulsions, where smaller amounts of sensitizing dye will, in many instances, give satisfactory or optimum sensitization. The optimum concentration, as discussed herein, of a sensitizing dye, namely the concentration at which the apparently greater sensitivity occurs, can also be determined in any conventional manner known to those skilled in the art by measuring the sensitivity of a series of emulsions containing different concentrations of the sensitizing material.

We wish to point out, however, that when our polyammonium salts are incorporated into a spectrally sensitized emulsion (as contrasted to an unsensitized emulsion), it is desirable that the sensitizing dye be compatible with our polyammonium salt.

For this reason, as spectral sensitizers (sensitizing dyes), we would employ only those which are substantially non-acidic. As non-acidic sensitizing dyes, we include all the known neutral and basic sensitizing dyes, and it is to be understood that our invention is not restricted in this respect. Examples of some of the non-acidic sensitizing dyes are the sensitizing cyanine dyes (see, for example. United States Patents 1 846,300; 1,846,301; 1,846,302; 1,846,303 and 1,846,304, each dated February 23, 1932; United States Patent 1,861,836, dated June 7, 1932; United States Patent 1,939,201, dated December 12, 1933; United States Patent 1,942,854, dated January 9, 1934; United States Patent 1,957,869, dated May 8, 1934; United States Patent 1,962,124, dated June 12, 1934; United States Patent 1,969,446, dated August 7, 1934; United States Patent 1,973,462, dated September 11, 1934; United States Patent 1,990,507, dated February 12, 1935; United States Patent 2,094,580, dated October 5, 1937; United States Patent 2,112,140, dated March 22, 1938, and French Patent 757,813, published January 5, 1934), the sensitizing merocyanine dyes (see United States Patent 2,078,233, dated April 27, 1937; United States Patent 2,089,729, dated Au-

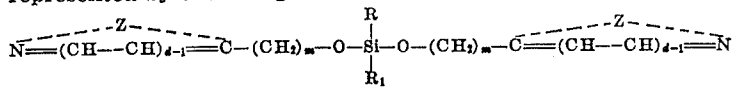
gust 10, 1937; United States Patent 2,153,169, dated April 4, 1939; and United States Patents 2,177,401, 2,177,402, and 2,177,403, dated October 24, 1939), the sensitizing hemicyanine dyes (see United States Patent 2,166,736, dated July 18, 1939) and the sensitizing hemioxonol dyes (see United States Patent 2,165,339, dated July 11, 1939, and French Patent 841,632, published May 24, 1939).

It is consequently apparent from the foregoing that our polyammonium salts may be incorporated in emulsions containing a large variety of different sensitizing dyes.

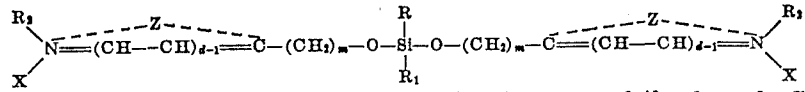
As already pointed out, our process is subject to considerable variation, particularly as respects the method of addition of our polyammonium salts, the type of photographic material treated (spectrally sensitized or not) and the nature of the material and amounts added. Our invention is useful for all types of optically sensitized emulsions, especially unsensitized emulsions of relatively low iodide content.

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

1. A bis-pyridyl compound selected from those represented by the two general formulas:

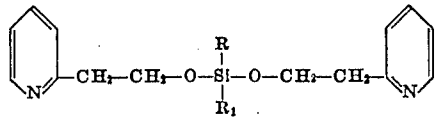


and



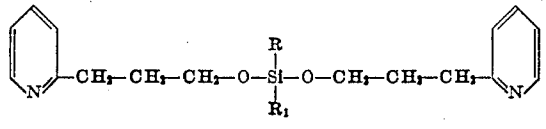
wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the pyridine series, R and R_1 each represents a member selected from the group consisting of an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 4, and a mononuclear aryl group of the benzene series, R_2 represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 5, m represents a positive integer from 2 to 3, d represents a positive integer from 1 to 2, and X represents an anion.

2. A bis-pyridyl compound selected from those represented by the general formula:



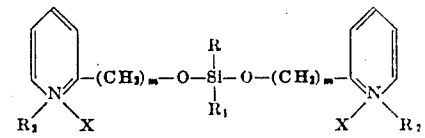
wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 4.

3. A bis-pyridyl compound selected from those represented by the general formula:



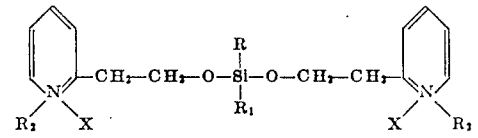
wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 4.

4. A bis-pyridyl compound selected from those represented by the general formula:



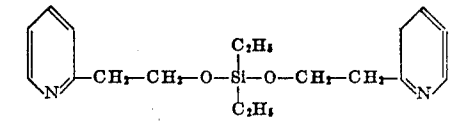
wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 4, R_2 represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 5, m represents a positive integer from 2 to 3 and X represents an anion.

5. A bis-pyridyl compound selected from those represented by the general formula:

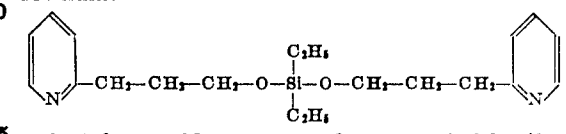


wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 4, R_2 represents an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 5, and X represents an anion.

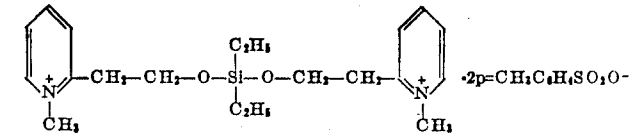
6. A bis-pyridyl compound represented by the formula:



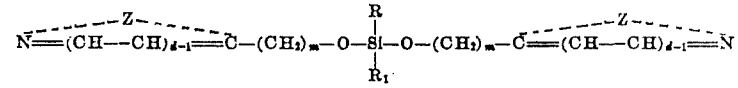
7. A bis-pyridyl compound represented by the formula:



8. A bis-pyridyl compound represented by the formula:

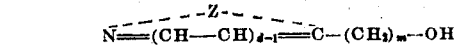


9. A process for preparing a bis-pyridyl compound selected from those represented by the general formula:

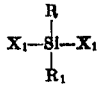


wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the pyridine series, R and R_1 each represents a member selected from the group consisting of an alkyl group of the formula C_nH_{2n+1} wherein n is a positive integer from 1 to 4 and a mononuclear aryl group of the benzene series, d represents a

positive integer from 1 to 2, and *m* represents a positive integer from 2 to 3, comprising reacting a compound selected from those represented by the general formula:

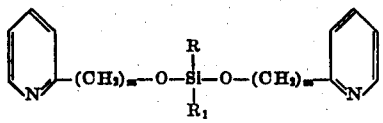


wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the pyridine series, *d* represents a positive integer from 1 to 2, and *m* represents a positive integer from 2 to 3, with a silane selected from those represented by the general formula:

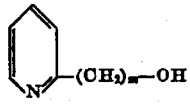


wherein R and R_1 each represents a member selected from the group consisting of an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4 and a mononuclear aryl group of the benzene series and X_1 represents a halogen atom in the presence of a tertiary organic amine.

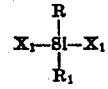
10. A process for preparing a bis-pyridyl compound selected from those represented by the general formula:



wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4 and *m* is a positive integer from 2 to 3, comprising reacting a compound selected from those represented by the general formula:

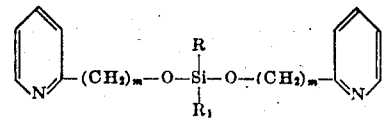


wherein *m* represents a positive integer from 2 to 3, with a silane selected from those represented by the formula:

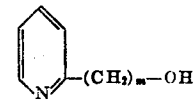


wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4 and X_1 represents a halogen atom in the presence of a tertiary organic amine.

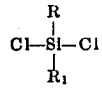
11. A process for preparing a bis-pyridyl compound selected from those represented by the general formula:



wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4 and *m* is a positive integer from 2 to 3, comprising reacting a compound selected from those represented by the general formula:

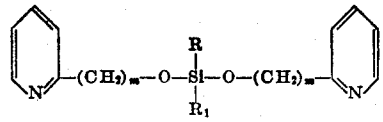


wherein *m* represents a positive integer from 2 to 3, with a silane selected from those represented by the formula:

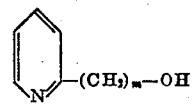


wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4, in the presence of a trialkyl amine.

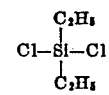
12. A process for preparing a bis-pyridyl compound selected from those represented by the general formula:



wherein R and R_1 each represents an alkyl group of the formula C_nH_{2n+1} wherein *n* is a positive integer from 1 to 4 and *m* is a positive integer from 2 to 3, comprising reacting a compound selected from those represented by the general formula:



wherein *m* represents a positive integer from 2 to 3, with a silane represented by the formula:



in the presence of a trialkyl amine.

CHARLES F. H. ALLEN.
DONALD M. BURNESS.

No references cited.

Certificate of Correction

Patent No. 2,500,110 March 7, 1950

CHARLES F. H. ALLEN ET AL.

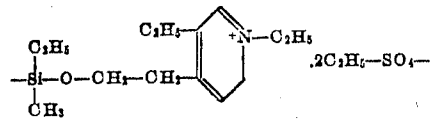
It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 6, line 12, for "-2-ethoxy]" read *-2) ethoxy]*; Example III, for that portion of the formula reading

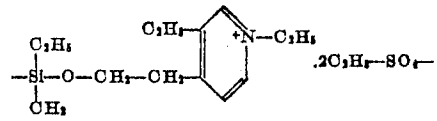


read

column 7, Example IV, second formula thereof, for that portion reading



read



Example V, in the formula, for "$CH_2{=}CH_2$" read *$CH_3{-}CH_3$*;

column 8, lines 38 to 40, inclusive, for



read

column 12, line 60, for that portion of the formula reading

".2p=CH_3" read *.2p−CH_3*

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of July, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.