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STABILIZATION OF ZINC FERRICYANIDE

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7 Claims. (Cl. 106—193)

This invention relates to zinc ferricyanide. It is an object of this invention to improve the stability of zinc ferricyanide against decomposition by light. A further object is to provide a sheet of paper coated with a binder comprising zinc ferricyanide and characterized by stability against loss of potency when handled in daylight or artificial light for long periods. Additional objects and achievements of this invention will become apparent as the description proceeds.

In my copending application Serial No. 674,039 filed July 25, 1957, I have discussed at length the art of preparing written or typed material in duplicate or multicopy by the aid of hectographic processes or by typing with one or more carbons, wherein the recent trend has been to use colorless "carbon" paper or stencils, the copied record to be developed into visible color after transfer of the recorded matter has been achieved. In said copending application I have further described and claimed as my invention base web material, for instance paper, coated on one side with a binder (e.g. starch) containing zinc ferricyanide in highly dispersed and uniformly distributed form. Such paper is adapted for use as copy paper for the aforementioned duplication processes, particularly where the colorless coloring agent on the "carbon" paper or stencil is a leuco triarylmethane compound, a triarylmethane carbinol, a lower alkyl ether of the latter, or a triarylmethane phthalide.

The coated copy paper thus produced is fairly stable and useful for practical purposes if it is stored inside a wrapper whereby light is excluded from the coated surfaces of the sheets or if it is stored in the dark. In use, however, the individual sheets are sometimes laid open and exposed to light for hours or days, and under these circumstances they are apt to become discolored. Such discoloration is generally symptomatic of decomposition of the zinc ferricyanide, and causes the sheet to lose its potency for developing leuco triarylmethanes, etc., into color.

Now, I have discovered that zinc ferricyanide may be stabilized against decomposition by light, particularly when in the form of a film or coating upon a sheet of paper, if it is modified by guanidine salts, chloride ions and excess zinc ions. By "modification" I mean that the zinc ferricyanide is either treated with water-soluble guanidine salts, zinc compounds, and chloride salts (or HCl), or it is initially synthesized in the presence of such compounds and salts.

The effect of the guanidine salt, zinc salt and chloride ions is not clearly understood. It is conceivable that the phenomenon is simply one of double salt formation between zinc ferricyanide and added zinc salt or the molecules of say, guanidine chloride, nitrate or sulfate. Or it is possible that part of the zinc in the zinc ferricyanide is replaced by the cationic radical of the guanidine salt.

In any event, I find that the light-stability of the coated sheet is immensely improved, if the zinc ferricyanide is admixed with or synthesized in the presence of (*a*) 2 to 12 moles of water-soluble guanidine salts,

(*b*) 12 to 2 moles of excess water-soluble zinc salts, and (*c*) a total of 40 to 10 moles of chlorides, for each mole of zinc ferricyanide.

As practical guanidine salts for the above purpose may be named guanidine chloride, guanidine nitrate and guanidine sulfate. The added zinc salts may be in the form of zinc chloride, zinc nitrate, zinc sulfate. Where the modification is achieved in the process of synthesis of the zinc ferricyanide, say from sodium or potassium ferricyanide and a water-soluble zinc salt, it is obvious that the range 12 to 2 moles of zinc salt above indicated is to be augmented by the extra stoichiometric quantity required for the synthesis.

The quantity of chloride ions to be added is calculated to allow for the quantity introduced via the chosen guanidine or zinc salt; if any additional quantity is required, it may be added in the form of sodium chloride, potassium chloride, ammonium chloride or hydrochloric acid.

Within the above broad ranges, optimum ratios of *a*:*b*:*c* may be selected for practical reasons, for instance according to the following table:

c	*b*	*a*
Moles of Cl ions	Moles of Zn ions	Moles of Gu ions
35	8 to 3	2 to 10
25	8 to 3	2 to 10
20	7 to 4	3 to 12
15	7 to 4	4 to 12
10	7 to 5	5 to 12

It will be seen from this table, that the quantity of guanidine ions is preferably raised when the quantity of excess zinc is near its lower limits, and vice versa.

Processwise, the modification is effected simply by adding said salts to an aqueous suspension of zinc ferricyanide, or by adding aqueous solutions of said salts to the aqueous reaction mass in which the zinc ferricyanide is produced, and holding the mixture at room temperature for an optional period, say 15 minutes to 2 hours. The end of the reaction is recognized by a change in shade, from reddish yellow to a greener yellow shade, in the zinc ferricyanide initially added or precipitated in the reaction mass.

The resulting aqueous suspension may be used directly (that is without filtering off the modified zinc ferricyanide), for producing coatings upon paper, after thickening said aqueous suspension with a suitable binder such as starch. The coating itself may be achieved by spraying, brushing or by the aid of rollers. Fillers, humectants and other desirable agents may be incorporated into the paste. Coloring materials other than leuco triarylmethanes may be incorporated for shading purposes, or for the purpose of providing a contrasting background color.

For the purpose of judging the stability of the zinc ferricyanide coating, an empirical scale has been adopted wherein the rating is expressed by a digit from 0 to 6, 0 being very poor, while 6 indicates excellent stability (no change after exposure for 30 minutes in the Fade-Ometer). Ratings of 4 to 6 are considered satisfactory for practical purposes.

Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

I. STABILIZATION AFTER FORMATION OF THE ZINC FERRICYANIDE DISPERSION

A dispersion of zinc ferricyanide containing 0.001 mole

of zinc ferricyanide per 10 parts total is prepared as follows:

43 parts (0.31 mole) of zinc chloride dissolved in 400 parts of water is added to a solution of 44 parts (0.133 mole) of potassium ferricyanide also dissolved in 400 parts of water.

The resulting precipitate is filtered off on a Büchner funnel, washed with water and then redispersed in water (670 parts) so that each 10-part aliquot contains 0.001 mole of zinc ferricyanide.

Stabilization of the zinc ferricyanide to light is demonstrated in the following examples:

Example 1

To a 10-part aliquot of the above dispersion are added 0.40 part (0.004 mole) of guanidine hydrochloride and 1.08 parts (0.008 mole) of zinc chloride. After standing for approximately 30 minutes with occasional agitation, the dispersion turns a lighter yellow color. About three parts of a 12.5% (by weight) starch solution is added and the dispersion is coated on paper. When this coating is exposed in the Fade-Ometer for 30 minutes, essentially no change is observed from the unexposed portion, while the original zinc ferricyanide (i.e. with no addition of guanidine hydrochloride) became a dull blue color in the same exposure time.

The rating of the above product on the mentioned stability scale is 5.

Example 2

To a 10-part aliquot of the zinc ferricyanide suspension prepared hereinabove, are added 0.50 part (0.004 mole) of guanidine nitrate, 0.59 (0.002 mole) of zinc nitrate hexahydrate and 1.1 parts (0.015 mole) of potassium chloride. After approximately two hours, the dispersion turns to the lighter yellow shade and is coated on paper, again using starch as a binder, as in Example 1. Only a slight change in appearance is observed after exposure of the coating for 30 minutes in the Fade-Ometer. Its rating on the stability scale is 4.

Example 3

To a 10-part aliquot of the above suspension of zinc ferricyanide is added 0.80 part (0.008 mole) of guanidine hydrochloride and 0.28 part (0.002 mole) of zinc chloride. The yellow stable modification of zinc ferricyanide gradually forms and, after standing approximately two hours, about three parts of a 12.5% starch solution is added, and the dispersion coated on paper. When the coating is exposed in the Fade-Ometer for 30 minutes, only a slight change in appearance is observed.

Example 4

To 10 parts of of an aqueous suspension containing 0.001 mole of zinc ferricyanide is added 1.0 part (0.010 mole) of guanidine hydrochloride and 1.08 parts (0.008 mole) of zinc chloride. After standing for approximately 30 minutes, the dispersion turns to the greener yellow shade of stabilized zinc ferricyanide, and is coated on paper again using about three parts of 12.5% starch solution as the binder. Fade-Ometer exposure for 30 minutes shows very little change in appearance of the zinc ferricyanide coating. (Stability rating=5.)

In place of starch as the binder in all of these and subsequent examples, other binders such as polyvinyl alcohol, methyl-cellulose, carboxymethylcellulose, and modified starches, e.g. acetylated starch, may be used.

II. STABILIZATION BY ADDITION OF GUANIDINE HYDROCHLORIDE TO POTASSIUM FERRICYANIDE SOLUTION BEFORE PRECIPITATION OF ZINC FERRICYANIDE

In the following examples, guanidine hydrochloride, as listed in Table I, is added to 5.0 parts of a potassium ferricyanide solution containing 0.66 parts (0.002 mole) of potassium ferricyanide. Forty-three hundredths part (0.003 mole) of zinc chloride is required to precipitate the above amount of ferricyanide to give 0.001 mole of zinc ferricyanide. Listed in the table is the amount of zinc chloride used in excess of the 0.003 mole required. The total amount of zinc chloride is dissolved in 5.0 parts of water. The total amount of chloride ion from the guanidine hydrochloride and from the zinc chloride, as well as any additional amount of chloride ion, added as concentrated hydrochloric acid, is also listed in the table. The zinc chloride solution is added to the ferricyanide solution with stirring. The dispersion is allowed to stand for approximately one hour; about two parts of 12.5% starch solution is added; and the mixture is coated on paper and dried. The coating is exposed in the Fade-Ometer for 30 minutes and the stability rating is assigned to the coating based on the degree of change visually noted.

TABLE I

Test No.	Guanidine Hydrochloride		Excess Zinc Chloride (95% Purity)		Hydrochloric Acid Mols	Equiv. Chloride Ion Total Mols	Stability Rating
	Wt. (pts.)	Mols	Wt. (pts.)	Mols			
1	0.193	0.002	0.57	0.004	0.006	0.022	5
2	.193	.002	1.00	.007	-------	.022	5
3	.290	.003	0.29	.002	0.022	.035	4-5
4	.290	.003	0.57	.004	-------	.017	5-6
5	.290	.003	1.14	.005	-------	.025	5
6	.39	.004	1.00	.007	-------	.024	5
7	.67	.007	0.57	.004	0.014	.035	5
8	.78	.008	1.00	.007	-------	.028	5
9	.96	.010	0.29	.002	0.015	.035	4
10	.96	.010	0.43	.003	-------	.022	6
11	.96	.010	1.00	.007	-------	.030	5

III. STABILIZATION BY ADDITION OF GUANIDINE HYDROCHLORIDE TO ZINC CHLORIDE SOLUTION

To a solution of 1.1 parts (0.00334 mole) of potassium ferricyanide in 5.0 parts of water is added a solution containing 1.75 parts (0.012 mole, 95% purity) of chloride and 1.4 parts (0.0146 mole) of guanidine hydrochloride in 5.0 parts of water. After standing a few minutes, the greener yellow stable precipitate forms. About 5 parts of 12.5% starch solution is added to the dispersion and the dispersion coated on paper and dried. This yellow colored paper presents a very reactive surface and readily converts carbons of leuco triarylmethane dye derivatives to the dye.

IV. USE OF A FILLER

The yellow color of paper coatings of zinc ferricyanide may be greatly reduced by the addition of fillers to the dispersion. A preferred procedure is the following: To a solution of 11 parts (0.0334 mole) of potassium ferricyanide dissolved in 50 parts of water is added a solution of 17.5 parts (0.12 mole) of zinc chloride and 14.0 parts (0.146 mole) of guanidine hydrochloride in 50 parts of water. The dispersion of zinc ferricyanide turns to the stable greener yellow form within a few minutes after the formation of the precipitate. One hundred parts of a 12.5% starch solution and 100 parts of titanium dioxide are added. The resulting light-cream colored dispersion is homogenized for a few minutes with an Eppenbach mixer and then coated on paper and the paper dried. The paper obtained presents a very light-yellow colored surface and is an effective copy paper for carbon papers, as described earlier. In this formulation, the ratios of mole equivalents of excess zinc, guanidine and chloride ions to the zinc ferricyanide formed are as follows: 8.75:4.8:24.5:1. On exposure of the coating for 30 minutes in the Fade-Ometer, little change in appearance is observed.

In place of titanium dioxide, other filler materials, such as English china clay or barium sulfate, may also be used.

It will be understood that the details of the above examples may be varied widely within the skill of those engaged in this art.

I claim as my invention:

1. A process of stabilizing zinc ferricyanide against decomposition under the action of light, which comprises modifying the same by the aid of ionizable, water-soluble guanidine salts and zinc salts in the presence of chloride ions, the quantities of said salts being sufficient to supply from 2 to 12 moles of guanidinium ion and from 12 to 2 moles of excess zinc ion, and the quantity of chloride ions present being from 40 to 10 moles, per mole of $Zn_3[Fe(CN)_6]_2$.

2. A process as in claim 1, the modification being achieved by adding said salts to an aqueous suspension of zinc ferricyanide.

3. A process as in claim 1, modification being achieved by adding aqueous solutions of said salts, in addition to a stoichiometrically required quantity of a water-soluble zinc salt, to an aqueous solution of potassium ferricyanide, whereby to modify the zinc ferricyanide directly as it is synthesized.

4. A process of stabilizing a coating of zinc ferricyanide on a sheet of paper against discoloration when exposed to light, which comprises incorporating into the coating zinc ferricyanide modified as defined in claim 1.

5. A sheet of paper coated on a face thereof with a coating of modified zinc ferricyanide, said modification being as defined in claim 1.

6. A sheet of paper coated on a face thereof with a coating of a modified zinc ferricyanide as defined in claim 1, said coating containing further a binder selected from the group consisting of starch, polyvinyl alcohol, methyl-cellulose, carboxymethyl-cellulose and acetylated starch.

7. A sheet of paper coated on a face thereof with a coating of a modified zinc ferricyanide as defined in claim 1, said coating containing further a filler selected from the group consisting of titanium dioxide, barium sulfate and English china clay.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,978,345 April 4, 1961

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 33, after "0.59" insert -- part --; line 52, strike out "of", second occurrence; column 4, line 42, before "chloride" insert -- zinc --.

Signed and sealed this 22nd day of August 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents