

1

3,411,936

DEVELOPING ELECTROSTATIC IMAGES WITH A LIQUID DEVELOPER CONTAINING TETRAPHENYL TIN OR ZIRCONYL 2-ETHYLHEXOATE

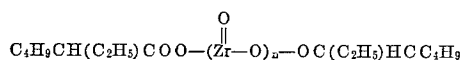
Jerome Roteman, Freehold, N.J., and Beatrice Arnovich, New York, N.Y., assignors to Interchemical Corporation, New York, N.Y., a corporation of Ohio

No Drawing. Filed Mar. 1, 1965, Ser. No. 436,328

4 Claims. (Cl. 117-37)

ABSTRACT OF THE DISCLOSURE

A method of liquid developing of negatively charged electrostatic images which involves imparting a positive charge to pigment particles in the liquid developer by means of a charge control agent selected from the group consisting of tetraphenyl tin or zirconium complex salt



where n is between 1 and 2.

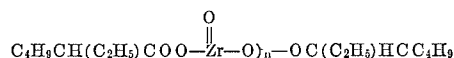
This invention relates to electrostatic printing and copying. More particularly, it relates to a method of developing electrostatic images using an improved liquid developer.

One typical conventional electrostatic printing process includes coating a surface of a relatively conductive backing member with a photoconductive insulating material such as selenium, anthracene, or sulfur, and then providing an electrostatic charge of a given potential on the surface of the photoconductive coating. Then, a light image is focused on the charged surface discharging or lowering the potential of the irradiated areas, while leaving the remainder of the surface in a charged condition, thereby forming an electrostatic image. The electrostatic image may be rendered visible by the application of developer liquid or powder which is held electrostatically in the charged areas in the case of positive images, or, in the case of reversal type images, the charge on the developer is such that the developer is repelled from the charged areas and deposits in discharged areas. The developed image is then transferred and fixed to another surface. A more detailed description of such a conventional process may be found in U.S. Patent No. 2,297,691 to C. F. Carlson. A variation in the electrostatic printing process in which the intermediate step of transferring the developed image is eliminated and the developed image is produced directly upon the desired surface is described in U.S. Patent 3,052,539 to H. G. Greig.

We have now found an improved method of liquid developing of negatively charged electrostatic images which are the standard electrostatic images in the processes described above. Our method is particularly effective in the direct image method of electrostatic printing described in the Greig patent. The method may be considered to be an improvement over the conventional methods of liquid developing described in Patents Nos. 3,078,231 and 2,907,674 to Metcalfe et al. These patents describe electrostatic liquid developers comprising pigments dispersed in electrically insulating liquids containing control agents. These control agents which are absorbed on the surface of the pigment particles impart to the particles electrical charges of selected polarities. For example, the patents set forth that boiled linseed oil acts as a control agent to impart a negative charge to the pigment particles while linseed oil modified alkyd resins act as control agents to impart a positive charge to the pigment particles.

2

The method of this invention involves the improvement of imparting a positive charge to pigment particles in such liquid developers by means of new control agents. We have discovered that the metallic soaps, tetraphenyl tin, and also the zirconium complex salt:



(where n is between 1 and 2) will impart positive charges to the pigment particles of the Metcalfe patents in the electrically insulating liquids of the Metcalfe patents.

The pigments may be any of the pigments used in Patent No. 2,907,604. In order to illustrate the best embodiment of this invention, black and white copies, carbon black is the only pigment used in the illustrative examples. However, the substitution of any of the conventional pigments described in said patent should be obvious. While the pigment particles are usually hetero-charged, that is they may have combined negative and positive charge, the action of our new charge control agents would be sufficient to offset any negative charge that the pigment particles may have obtained during preparation or under other circumstances.

Our new charge control agents are used in amounts sufficient to impart a positive change to the pigment particles. The quantity of charge control agent necessary will vary with the nature of the charge already on the pigment. An individual determination may be made for each new combination of charge control agent and pigment. In each case a series of developer compositions is prepared with increasing amounts of charge control agent in accordance with the procedure of Example 1. These are tried in the selected formulation in the order of increasing amounts of charge control agent. The amount of charge control agent which gives a faint image is regarded as the minimum amount necessary to produce an image.

Likewise the electrically insulating liquids used are the same as those described in the Metcalfe patents and conventionally used in the liquid developing art. The liquids have a high volume resistivity, e.g., toluene, cyclohexane, perchloroethane, Freon (a trade name of E. I. du Pont de Nemours & Co. for various fluorinated compounds) n-pentane and carbon tetrachloride. While the examples which follow, use an aliphatic solvent having a boiling range of 315-350° F., any of the conventional electrically insulating solvents will be operable in the method of this invention.

By metallic soaps, we mean metallic, especially alkaline earth- and heavy-metallic salts of fatty acids containing at least 6-7 carbons and including naphthenic acid which is a cyclic aliphatic acid. Among the most effective charge control agents in the practice of this invention are the salts of naphthenic and octanoic acids including copper, cobalt, magnesium, manganese, iridium, cadmium, silver, potassium, titanium, cerium, zirconium, lithium and nickel naphthenates as well as zirconium, ferric, sodium, zinc, cobalt, silver, potassium, cadmium, manganese and magnesium octoates. The terms octanoic acid and octoates as used in this description are meant to be broad enough to respectively cover the eight carbon 2-ethyl hexanoic acid and 2-ethyl hexanoates. Other metallic soaps such as lead, cobalt or manganese tallates, soyates or linoleates may also be used.

While the method of this invention does not require the use of resinous binders in the developer, and copies of excellent clarity and intensity are produced without such binders, a resinous binder will increase the rub-resistance of the printed copies. The resinous binder is preferably substantially uncharged since a charge on the binder may interfere with the metallic control agent imparting a positive charge on the pigment particles. However, the charge

control agents impart a sufficient charge to offset any small charge which the binder may have. The binder may be any conventional binder used in both liquid and dry electrostatic developers. Examples of such binders are epoxy resins made by the reaction of Bisphenol A and epichlorohydrin, polyterpenes, polyvinyl acetate, polystyrene and polyethylene.

We have found it to be very preferable in the practice of the method of this invention for the developer used in this invention to be free from drying oils including even resins containing incorporated drying oils. In the developing apparatus, the developer composition may stand in its reservoir exposed to the atmosphere for days and even weeks before being replaced or used. The developer should be stable under these circumstances. It is apparent to us that the drying oils, particularly in presence of the metallic soaps used as control agents, cause the developers to become unstable and flocculate. This results in poor and inconsistent images when the developer is used. We also believe that the poor quality of the images may be due to a reduction in the effectiveness of the metallic soap as a charge control agent in the presence of drying oils. Most metallic soaps are known driers for drying oils. That is, the soaps assist in the oxidation of the drying oil. The functioning of the metallic soap as a drier for the drying oil appears to interfere with the function of the soap as a charge control agent.

The proportions of the pigment and the electrically insulating liquids are preferably the same as in U.S. Patent No. 2,907,674.

Preferably, sufficient salt is used to provide from 10^{-5} to 10^{-1} parts of metal for each part of pigment. If a resinous binder is used, preferably 0.25 to 7 parts of resin are present for each part of pigment. It should be noted that unless otherwise specified, all proportions in this specification and claims are by weight.

The following examples will illustrate the practice of this invention:

Example 1

The following composition is milled on a two-roll mill at 150° F. for 15–20 minutes and then jet-milled to a 20 micron particle size:

	G.
Carbon black	0.02
Epon 1007 (An epoxy resin which is the reaction product of epichlorohydrin and Bisphenol A (di-hydroxyphenyl propane) having an epoxide equivalent weight of 1500–2000, an average molecular weight of 2625 and from 1.3 to 1.7 epoxides per molecule.)	0.08

The resulting particles are then dispersed in 100 cc. of Isopar G. (an aliphatic hydrocarbon solvent having a boiling range of $315\text{--}350^{\circ}$ F. and a K.B. value of 27).

Then an electrostatic copying sheet prepared in accordance with Example 1, U.S. Patent No. 3,052,539 is charged negatively by subjecting it to a corona discharge and then exposed to a light image to produce a negatively charged electrostatic image on the surface of copying sheet in accordance with the procedure of Patent No. 3,052,539.

In an attempt to develop the electrostatic image into a visible image, the copying sheet bearing the charged image is submerged in the above dispersion for about 6 seconds. No readable image is produced.

The above procedure is repeated using the same ingredients, proportions and conditions except that in place of the developer composition, there are used a series of developer compositions having the identical composition of the original developer but with the addition of 0.5×10^{-3} , 1.0×10^{-3} , 1.5×10^{-3} , 2.0×10^{-3} , 3.0×10^{-3} , 4.0×10^{-3} and 5.0×10^{-3} grams of zirconium as zirconium naphthenate to the composition of the series. It is found that even the addition of 0.5×10^{-3} grams results in the development of a faint black visible image and that

1.5×10^{-3} g. of zirconium or greater result in sharp, clear and intense black visible images.

Example 2

A cross-linked epoxy resin is prepared by heating a mixture of 100 parts of an epoxy resin which is the reaction product of epichlorohydrin and Bisphenol A and has an epoxide equivalent weight of about 365 and an average molecular weight of 700 and 2 parts of diethylene triamine at 150° F. under mild agitation for 18 hours. The final product is sufficiently cross-linked to raise the melting point of the resin from 104° F. to 172° F.

0.055 g. of the cross-linked resin, 0.025 g. of Epon 1007 and 0.02 g. of carbon black are then milled on a two-roll-mill at 150° F. for 15–20 minutes and then jet-milled to a 20 micron particle size.

The resulting mixture is then dispersed in 100 cc. of Isopar G.

Then the procedure of Example 1 is repeated using the same additives, conditions and proportions except that the above dispersion is used in place of the developer composition of Example 1. The results are substantially the same as in Example 1.

Example 3

Example 2 is repeated using the same procedure, ingredients, proportions and conditions except that the additive is iron as ferric naphthenate. The addition of at least 0.7×10^{-3} g. of iron results in a sharp, clear and intense black image equivalent to that of Example 2.

Example 4

Example 2 is repeated using the same procedure, ingredients, proportions and conditions except that the additive is sodium as sodium naphthenate. The addition of at least 1.6×10^{-6} g. of sodium results in a sharp, clear and intense black image equivalent to that of Example 2.

Example 5

Example 2 is repeated using the same procedure, ingredients, proportions and conditions except that the additive is zinc as zinc octoate. The addition of at least 2.6×10^{-3} g. of zinc results in images almost equivalent to those of Example 2.

Examples 6 through 15

Example 2 is repeated following the same procedure and using the same ingredients and proportions as in Example 2 except that the following additives are used in place of zirconium naphthenate:

Example	Additive	Minimum quantity of metal necessary to produce a sharp positive readable image, g.
6.....	Cerium Naphthenate.....	5.5×10^{-3}
7.....	Cobalt Octoate.....	5.0×10^{-3}
8.....	Cobalt Naphthenate.....	2.0×10^{-3}
9.....	Titanium Naphthenate.....	4.4×10^{-4}
10.....	Potassium Naphthenate.....	2.0×10^{-3}
11.....	Silver Naphthenate.....	2.5×10^{-3}
12.....	Cadmium Naphthenate.....	3.8×10^{-3}
13.....	Iridium Naphthenate.....	1.2×10^{-4}
14.....	Manganese Naphthenate.....	1.1×10^{-4}
15.....	Magnesium Naphthenate.....	6.5×10^{-3}

Example 16

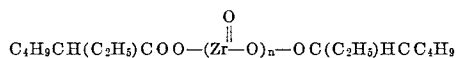
0.05 g. of carbon black is dispersed in 100 cc. of Isopar G. solvent.

Then an electrostatic copying sheet prepared in accordance with Example 1 U.S. Patent No. 3,052,539 is charged negatively by subjecting it to a corona discharge and then exposed to a light image to produce a negatively charged electrostatic image on the surface of copying sheet in accordance with the procedure of Patent No. 3,052,539.

In an attempt to develop the electrostatic image into a visible image, the copying sheet bearing the charged image

is submerged in the above dispersion for about 6 seconds. No readable image is formed.

The above procedure of this example is repeated using the same ingredients, proportions and conditions except that in place of the above composition, a composition of 5 g. of carbon black and 2.9×10^{-5} g. of zirconium as



(where n is between 1 and 2) made in accordance with U.S. Patent 2,739,905, particularly Example 1 of said patent in 100 cc. of Isopar G. solvent is used. A clear, sharply defined and visible image is produced.

Example 17

The following developer composition:

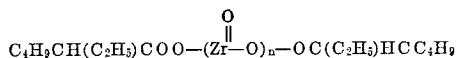
	G.
Carbon black	0.02
Flushed alkali blue	0.02
Polyterpene resin	0.5

is dispersed in 100 cc. of Isopar G. (an aliphatic hydrocarbon solvent having a boiling range of 315–350° F. and a K.B. value of 27).

Then an electrostatic copying sheet prepared in accordance with Example 1, U.S. Patent No. 3,052,539 is charged negatively by subjecting it to a corona discharge and then exposed to a light image to produce a negatively charged electrostatic image on the surface of copying sheet in accordance with the procedure of Patent No. 3,052,539.

In an attempt to develop the electrostatic image into a visible image, the copying sheet bearing the charged image is submerged in the above dispersion for about 6 seconds. A very vague and unclear image results.

The above procedure of this example is repeated using the same ingredients, proportions and conditions except that in place of the above composition, a composition of 0.02 g. carbon black, 0.02 g. of flushed alkali blue, 0.5 g. of polyterpene resin and .09 g. of zirconium as



(where n is between 1 and 2) made in accordance with U.S. Patent 2,739,905, particularly Example 1 of said patent in 100 cc. of Isopar G. solvent is used. A clear, sharply defined and visible image is produced.

Example 18

Following the procedure of Example 1, a white developer composition is prepared from the following components:

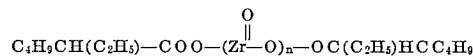
Parts by weight

Cocoonut oil	15
Zinc oxide (photoconductive)	26
Solution of cobalt naphthenate in toluene (cobalt content—1%)	1
Solution of manganese in toluene (manganese content—1%)	1
Toluene	20

Following the developing procedure of Example 1 a readable white image is produced.

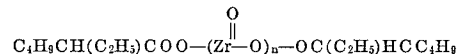
We claim:

1. In the method of electrostatic printing, in which a developing composition comprising a dispersion of pigment in an electrically insulating liquid is applied to a surface carrying a negatively charged electrostatic image, the improvement of dissolving in said insulating liquid at least one member selected from the group consisting of tetraphenyl tin and



where n is a fraction between 1 and 2, said member being present in an amount from 10^{-5} to 10^{-1} parts by weight of metal per part by weight of pigment sufficient to impart a positive charge to the pigment particles.

2. The method of claim 1 wherein said member is



3. The method of claim 1 wherein said member is tetraphenyl tin.

4. The method of claim 1 wherein said insulating liquid further contains a substantially uncharged binder resin.

References Cited

UNITED STATES PATENTS

2,584,041	1/1952	Nowak et al.	106—310
2,739,905	3/1956	Mack et al.	106—310
2,793,962	5/1957	Collins et al.	106—310
2,807,553	9/1957	Fischer	106—310
2,907,674	10/1959	Metcalfe et al.	117—37
3,102,045	8/1963	Metcalfe et al.	117—37
3,141,793	7/1964	Oliphant	117—37
3,215,527	11/1965	Johnson	117—37
3,231,374	1/1966	Sciambi	117—37
3,241,957	3/1966	Fausser et al.	117—37
3,251,688	5/1966	Mihajlov	117—37
3,259,581	7/1966	Matkan	117—37
3,320,169	5/1967	East et al.	252—62.1

WILLIAM D. MARTIN, *Primary Examiner*.

E. J. CABIC, *Assistant Examiner*.