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PHOTOSENSITIVE MATERIALS

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This invention relates to diazotype processes and specifically provides photosensitive diazotype materials, coated with substantially insoluble metal fluorides in finely divided form, prior to or concurrently with the application of a conventional sensitizing composition to said materials.

The invention further relates to a method of preparing such diazotype materials.

Photosensitive diazotype materials generally comprise a support or base which may be paper, cardboard, cellulose film, textile fabric, or other suitable sheet material, coated with a diazonium salt composition sensitive to light and actinic rays. During a so-called developing process the salt is converted to a dye through the action of a bonding or coupling agent which may be mixed with the salt composition or through the action of a developer.

One typical feature of diazotype materials is the high optical density of the lines in the image (hereinafter designated briefly by the term density), which is a function of the concentration of diazonium salt. Increased density results in greater contrast and hence more legible final picture or print.

The maximum density of a diazo material depends directly on the exposure time which has to be used in order to get a satisfactory print. In the ensuing disclosure I shall designate as the "sensitivity" of the material, the reciprocal of said exposure time. Generally speaking, the sensitivity of conventional diazo materials decreases with increase in the maximum density of the material.

It is an object of this invention to make it possible to increase the density of the image formed by a diazotype without reducing the sensitivity of the material. Another object is to enable more highly diluted sensitizing salts to be used while retaining an equal density and a higher sensitivity than that of conventional sensitizing solutions that do not incorporate finely divided insoluble metal fluorides according to the invention.

When an area of maximum density on a developed printed copy is microscopically examined under moderate magnification it is found that the elementary areas of the surface fibres have a lower density than that of the elementary surfaces of the inter-fibre interstices. This is because the opacifying dye formed on development occurs primarily (insofar as the surface fibres are concerned) inside the body of the fibre and consequently leaves the specular (i.e. mirror-like) reflection properties of the fibre partially unimpaired. In the interstices however the formed dye coats the underlying fibres entirely. When metal fluorides are used according to the invention it is found that the degree of specular (or mirror-type) reflection of the fibre drops. This drop in specular reflection can be readily observed by altering the incidence angle under which the print is illuminated.

In conventional diazotype materials containing no metal fluorides, the maximum density is found to be much lower when the print is illuminated with direct front rays

normal to the surface of the print, than under lateral illumination. The difference is greatly reduced in the case of diazotype material containing metal fluorides according to the invention. Since a print is always observed under diffuse lighting with incident rays from many directions, it is obvious that inasmuch as the copy has reduced specular reflection it will also possess a higher over-all density than that of a copy having marked specular reflective properties.

Moreover the finely divided condition of the metal fluorides of the invention makes possible a much more thorough division of the dye formed on printing and development of the diazotype material, so that a given quantity of absorptive material coating a given surface area will absorb to a greater degree due to its more finely divided state.

It must be noted however that finely divided pigments such as zinc oxide, barium sulfate, titanium white, and the like, are not suitable for the purposes of the invention since they will coat the surface of the carrier with a white coating which reduces the maximum density of i rather than premanently bonding the dye to the surface of the carrier in a form capable of absorbing the incident light and hence reducing the degree of specular reflection of the fibres.

Moreover, while the use of conventional sub-layers o the type containing silica, alumina or any of various synthetic resins, does reduce to a certain extent the amoun of specular reflection, such substances however are less efficient than are the metal fluorides of the invention and result in diazotype materials that lack homogeneity, and are more expensive and difficult to produce.

It should be understood that the attempts at theoretica explanation given above are primarily included herei with the object of facilitating the comprehension of th present invention, but that my invention itself is not dependent for its value on the truth of any such explanations, since it is an experimental fact that the use of finely divided insoluble metal fluorides according to the invention substantially increases the real or apparent maximun density of diazotype materials without reducing the sensitivity thereof. The amount of such density increas depends on the size of the grains of the metal fluorid material used. Where the average grain diameter is abov one or two microns the density increase is comparativel low, and said increase is particularly high when the grain are within a range of average diameter from about 0.0 micron to about 0.50 micron. Below this range, i.e. wit grain size less than about 0.01 micron the increase i absorption still remains quite high but the surface become less mat.

According to the invention any metal fluoride may b used providing it is substantially insoluble in water, an especially the fluorides of the following metals: calciur barium, strontium, magnesium, aluminium, zinc, all in finely divided state.

Such finely divided insoluble metal fluorides can b prepared by reacting a compound of the metal dissolve or suspended in water, e.g. a chloride, a sulfate, a nitrat a hydroxide etc. with a compound containing a fluorid anion such as sodium fluoride, potassium fluoride, ammonium fluoride, hydrofluoric acid gas or solution an the like. Alternatively one or more of the constituent may be reacted in gaseous form.

The preferred method of my invention is to precipitate the metal fluoride in water and regulate the reactio conditions in regard to temperature, time and concentrations, in such a manner as to obtain a suspension c a particle size largely within the preferred range specified above, that is 0.01 to 0.50 micron. If necessary th resulting reaction product may be purified by filtratio dialysis, settling or other suitable procedure. A colloi inding mill may be used if desired in order to disperse ıy agglomerates of the particles that may tend to form.

The metal fluorides may be used separately or in adixture, e.g. zinc fluoride and/or calcium fluoride; aluinium fluoride and/or calcium fluoride, zinc and aluinium fluorides and so on. Best results have been obined when using calcium fluoride and/or zinc fluoride parately or together. The metal fluorides may be used solid form, as powders, and dispersed in the sensitizig solution by means of a colloid grinder mill for exmple. Or they may be added in the form of a conentrated colloidal aqueous solution to the sensitizing olution, also in a concentrated solution, so that the adition of the fluorides will permit a readjustment of the oncentration of said sensitizing solution to the desired alue.

Another procedure is to deposit the metal fluorides on ıe carrier or base of the diazotype material in an inial pre-coating step prior to exposure. The otherwise onventional pre-coating solution used may then contain om about 1% to about 25% of metal fluorides dependig on the strength of the desired effect, the convenience f using a concentrated solution and on economical conitions. Solutions containing from about 3 to about 10% y weight of fluoride appear to be most satisfactory in ıese various respects.

The solution used may further contain in addition to ıe fluorides other substances such as stabilizers, e.g. ıio-urea, naphthalene trisulfonic acid, 1, 3, 6; citric cid; tartric acid, boric acid, phosphoric acid, etc.; it ıay contain a part of the coupling or bonding agents, .g. diazonium salts, wetting agents, e.g. saponine; coloids, e.g. gelatine, gum-arabic, starch; developing-accelrators, e.g. glycerine, glycol; and dispersed resins e.g. rea-formol, thio-urea formol, dicyanodiamine-formol, olyvinyl acetate, and the like.

After the first layer has been dried the sensitizing soluon is applied to the carrier or base in the conventional ıanner. The sensitizing composition may include the iazonium salts described in French Patents Nos. ,096,363, 1,096,744 and 1,097,264, which salts include ıe diazonium derivatives of the compounds derived from ny of the folowing compounds: para-hydroxyethyl-ethl-amino-aniline; para-ethyl-amino-ortho-toluidine; paraiethyl-amino-aniline; para-amino-diphenyl-amine; paraenzyl-ethyl-amino-aniline; and others. These comounds may be used in their stabilized form, e.g. in the orm of double salts of zinc chloride, tin chloride, chloobenzenic sulfonate, and the like.

Any various coupler or bonding compounds may be sed to form the dyes with the diazonium salts on deelopment. Thus any of the following may be used ingly or in admixture: "R-salt," Schaeffer's salt, 2,3-diıydroxy-naphthalene-6 sulfonic acid; chloroglucinol, esorcinol, acetylacetanilide, and thers.

The metal fluorides may, .. an alternative procedure, e incorporated in the finely divided state, to the celluose pulp in the manufacture of the carrier paper sheet, referably together with the loading substances and in ny suitable proportions depending on the desired reults. The proportion may vary over the full range of rom 1 to 100% on the basis of the usual loading subtances (such as kaolin derivatives, barium sulfate, tianium oxide). However, a comparatively great proporion, say 20 to 90%, of the loading should preferably be etained in view of its function in opacifying the paper.

Alternatively or in addition, the divided metal fluorides nay be incorporated during any suitable stage of the paer-making process from the forming of the sheet to he final calendering step, by any suitable means such ıs surface treatment, or full immersion of the formed heet in a colloidal solution of the metal fluorides.

While the most usual carrier material is paper, other arrier sheet materials may be used such as cardboard, tracing paper, gelatine paper, coated paper, cellulose film, surface-saponified cellulose ester film and others.

The use of metal fluorides in the manner specified above imparts to photosensitive diazotype materials superior density and print-sensitivity as compared to identical materials when prepared without the incorporation of insoluble finely-divided metal fluorides or with such metal fluorides used in proportions outside the ranges specified. In addition to the advantages enumerated above, the use of the metal fluorides according to the invention increases the rate of the developing operation. Further, such use makes it possible to accomplish a greater uniformity of the bonding mixture where it is desired, for example, to obtain black. This is because the presence of the fluorides results in an attenuation in the colour variations with ambient conditions such as temperature obtaining during the ammonia developing process.

The ensuing examples are given to illustrate the invention but should not be construed as limiting the scope thereof. All parts are by weight unless otherwise specified.

Example 1

Calcium fluoride is dispersed in water by the following procedure. Equal volumes are mixed together of a first solution containing 5% anhydrous calcium chloride and a second solution containing 3.5% sodium fluoride. Instead of the second solution, there may be used a solution of 3% ammonium fluoride, or a 4.5% potassium fluoride solution. The resulting calcium fluoride precipitate is filtered off and is dispersed in water to obtain a concentration of 5% of calcium fluoride.

A sheet a base paper of a type conventionally used in diazotype process is coated with the dispersion in a diazotype coating machine. The sheet is allowed to dry and is then treated with any of the following sensitizing solutions conventionally used in diazotype processes:

Sensitizing solution I (providing blue lines):

Glycerol	cc	3
Tartric acid	g	3
Thio-urea	g	3
Zinc chloride	g	3
2,3-dihydroxynaphthaline-6-sulfonic acid	g	2
P-diazo-dimethylaniline	g	2
Water q.s. 100 cc.		

Sensitizing solution II (providing black lines):

Ethylene glycol	cc	3
Citric acid	g	5
Thio-urea	g	3
Zinc chloride	g	3
2,3 dihydroxinaphthalene	g	0.5
2,3 dihydroxynaphthalene-6-sulfonic acid	g	0.8
Acetoacetaniline	g	0.7
Phloroglucinol	g	0.1
P-diazo-(N-hydroxyethyl-N-ethyl)-aniline	g	2.8
Water q.s. 100 cc.		

Example 2

The procedure is identical with that in Example 1 except that an equimolecular quantity of zinc chloride (or alternatively zinc sulfate) is used in place of the calcium chloride.

Example 3

The same procedure is followed as in Example 1 except that one half the calcium chloride used is replaced by a molecularly equivalent quantity of zinc chloride (alternatively: zinc sulfate).

Example 4

The same procedure is followed as in Example 1 except that an aqueous suspension of calcium fluoride is used obtained by grinding a commercial grade of calcium chloride with water in a colloid mill to produce a suspension wherein a majority of the particles have a diameter smaller than one micron.

Example 5

A base paper sheet of the type used in diazotype processes is sensitized with either of the compositions indicated in Example 1, but modified by addition thereto of 5% zinc fluoride and/or calcium fluoride in fine powder form, and the solution is dispersed in a colloid grinder mill to a particle size of less than 1 micron.

Example 6

A base paper sheet of the type used in diazo-type processes is sensitized with a composition as indicated in Example 1, except that 75 cc. water are used instead of the 100 indicated in preparing the sensitizer solution and the solution is completed to 100 cc. by adding thereto a dispersion of zinc fluoride (and/or calcium fluoride) containing 20% metal fluoride, so as to obtain in fine a sensitizing solution containing 5% metal fluoride.

Example 7

The same procedure is used as in any of the Examples 1 to 6 except that the carrier or base used in a sheet of pigment-coated paper, e.g. baryta paper.

Example 8

One or more metal fluorides, such as calcium fluoride and/or zinc fluoride and/or magnesium fluoride, having a particle size within the above specified range are incorporated in a ratio of from 10% to 50% of dry extract in the conventional baryta-coating composition used in preparing so-called baryta paper. The resulting sheet of baryta paper is coated with a sensitizing solution as specified in Example 1.

Example 9

Base or carrier paper of the type used in diazotype processes for the so-called "semi-wet developing process" is pre-coated with a colloidal solution containing 4% calcium fluoride and 1.5% zinc fluoride, in which the two fluorides are first mixed with each other.

After the base sheet is dry the pre-coated surface is sensitized with a diazonium salt composition of the kind used in semi-wet developing processes, which composition may be as follows:

P-diazo-(N-benzyl-N-ethyl-amino)-aniline	g..	2
Tartric acid	g..	2
Gelatin	g..	1
Thio-urea	g..	2
Water q.s. 100 cc.		

The image is developed with a developer of the following composition:

Potassium carbonate	g..	2
Sodium borate	g..	2
Sodium hyposulfite	g..	3
Phloroglucinol	g..	0.3
Resorcinol	g..	0.3
Water q.s. 100 cc.		

Example 10

Paper of the type used in the semi-wet developing process is sensitized by immersion in a bath of the following composition:

A 6% water dispersion of calcium fluoride having a grain size less than 1 micron	cc..	100
1-diazo-4-benzoylamino-2,5-dimethoxy-benzene	g..	2.[illegible]
Monosonic phosphate	g..	2
1,3,6-naphthalene-trisulfonate	g..	3
Thio-urea	g..	2
Concentrated hydrochloric acid	cc..	1

The image is developed with a developer having the following composition:

Sodium formiate	g..	8
Sodium benzoate	g..	3
Thio-urea	g..	2
Phloroglucinol	g..	0.4
Resorcinol	g..	0.2

What I claim is:

1. A method of preparing a diazotype photosensitive material comprising first applying to a base material a finely divided water-insoluble fluoride of a metal selected from the group consisting of calcium, barium, strontium, magnesium, aluminum and zinc, and then coating the base material with a diazo salt and coupling agent.

2. A method of preparing a diazotype photosensitive material comprising first dispersing in a base material a finely divided water-insoluble fluoride of a metal selected from the group consisting of calcium, barium, strontium, magnesium, aluminum and zinc, and then coating the base material with a diazo salt and coupling agent.

3. A method of preparing a diazotype photosensitive material comprising first coating on the surface of a base material a finely divided water-insoluble fluoride of a metal selected from the group consisting of calcium, barium, strontium, magnesium, aluminum and zinc, and then coating the base material with a diazo salt and coupling agent.

4. A method as claimed in claim 1 wherein the fluoride is applied in a suspension containing 1–25% of the fluoride.

5. A method as claimed in claim 1 wherein the fluoride has a particle size of from about 0.5–1.0 micron.

6. A method as claimed in claim 2 wherein the base material is paper and said fluoride is integrated into a pulp composition which is processed to constitute said paper.

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