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LIGHT SENSITIVE DIAZOTYPE COMPOSITIONS CONTAINING SILICA PIGMENT

Joseph E. Frederick, Johnson City, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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The present invention relates to light sensitive diazotype materials, and especially to the use of a particular form of finely divided silica dispersed in the sensitizing solutions for said materials in order to enhance the density of the dye images produced in such materials.

The manufacture of the usual light sensitive diazotype materials involves the application to a fibrous base, such as paper, of a sensitizing solution containing as its main ingredients a light sensitive diazonium compound and an azo dye coupling component. In the processing of such materials they are exposed to light under a pattern to decompose the light sensitive diazonium compound where the light is transmitted by the pattern. Subsequently, a positive dye image is formed by coupling residual diazonium compound and azo coupler in an alkaline medium, preferably ammonia gas.

The ease and cheapness in the manufacture and processing of such materials speak for themselves, and have led to the growth of a substantial industry in the same. Yet, from its very inception this industry has been plagued by one facet of the manufacturing operation to which considerable effort has been contributed in order to find a solution.

It is manifest that the process being what it is dye image density is a direct function of the concentration of diazo in the image areas. It is equally manifest that the extent of destruction and, therefore, the printing speed will depend upon the availability of the diazonium salts to the transmitted light, i. e., the degree to which the diazonium salts accumulate and are retained at or near the surface of the base.

The very nature of the process of manufacturing the diazotype materials, however, is incompatible with such accumulation and retention of the diazonium salts at the base surface. Thus, the bases are generally fibrous in nature and the sensitizing components are applied thereto from an aqueous solution. Consequently, the components of the solutions strike into the base, thereby reducing their availability to the exposure light. In addition, by so striking through, they produce an image of low density and a sensitized material with a low printing speed.

This problem has been recognized for many years, and, in this connection, reference is made to British Patent 318,511, dated August 7, 1930, which, in referring to preparation of light sensitive diazotype material, states:

"Even when working very quickly, by for instance scraping away at once the excess of sensitizing solution, and quickly drying, the said solution penetrates to a fairly considerable depth into the thickness of the paper."

The British patentee suggested as a possible solution the coating of the base with a layer of gelatin and the application to the gelatin layer of the sensitizing components dissolved in low boiling solvents. It was his theory that the solvents would evaporate so quickly that the sensitizer would be retained on the surface of the gelatin. This proposal, involving as it does extra coating steps

and the use of expensive solvents, never received recognition by the industry.

Jahoda, U. S. P. 2,433,515, observed a somewhat analogous problem in connection with the manufacture of blueprint paper. Jahoda proposed as a solution the precoating of a sized paper with colloidal silica followed by application of the blueprint sensitizing solution. While this procedure is satisfactory for the blueprint industry, it is not for the diazotype industry, and this was admitted by the owner of the Jahoda patent in its publication entitled "Reproduction Paper Coating," H. P. Andrews Company, printed by J. E. Weiss & Son, Inc., New York, New York, 1951. This publication, on page 7 in discussing the precoat process of Jahoda states:

"The precoat processes for direct process paper are based on similar physical principles as the one for blueprint paper. Colloidal silica can also be used for direct process paper, but it has some disadvantages. Much better materials for precoating direct process papers are copolymers of synthetic resins in colloidal water solutions."

The disadvantages of Jahoda's method, as applied to direct process papers, are manifest. First, the laying down of the silica involves a separate coating operation which can be ill-afforded in the diazotype field. Again, the colloidal silica itself penetrates the base to a considerable depth, and because of its affinity for the sensitizer it carries the same into the base with it. Finally, colloidal silica, as available in aqueous dispersions, has a high content of iron which can be tolerated in blueprint but not in diazotype materials.

Von Glahn and Stanley, U. S. P. 2,566,709, realizing the disadvantages of Jahoda as applied to direct process papers, suggested the employment in the sensitizing composition itself of colloidal silica colloidally dispersed in said composition. This process eliminated the extra coating step of Jahoda, but failed to provide the desired result for a number of reasons. Thus, the problems of iron impurity and impregnation of the base with the colloidal silica still remained. Furthermore, the aqueous dispersion of the colloidal silica added to the sensitizing composition tenaciously retained the water in the pores thereof. As a result less than optimum quantities of sensitizer are absorbed to the silica grains due to the inability of the sensitizer to displace said water. Finally, the colloidal silica forms a continuous film of discrete particles on the base, giving rise to curl and brittleness. This method which, on its face, looked so promising was accordingly given short shrift.

At this point it appeared that the use of colloidal silica would never remove the plague from the industry. Sulich and Frederick in U. S. P. 2,662,013, issued December 8, 1953, finally departed from the use of such silica and recommended in lieu thereof non-colloidal silica comprising dehydrated silicic acid precipitated from aqueous solution and having a particle size ranging from 1 to 10 microns and a weight average particle size of 2 to 4 microns. Such silica was first added to the sensitizing composition. It was found, however, that while dye density was thus improved and the objections inherent in Jahoda and von Glahn and Stanley were eliminated a new snag was encountered. This involved the marked tendency of the silica to rub off the base on contact with other objects, thereby leading to deterioration of the dye image. This prompted these operators to use a binder to insure adhesion of the silica to the base. Unfortunately, the binders then available were incompatible with the sensitizing solution, and it was necessary to precoat the base with silica and binder and then apply the sensitizer. This not only injected an additional and unwanted coating step, but also gave rise to serious difficulties in maintaining the coating machines free from binder. It also complicated

the manufacturing procedure by bringing in an item having no direct bearing on the processing of light sensitive material.

A further effort to give the art a satisfactory key to the problem is reported by Kosalek and Sulich in their application Serial No. 363,398, filed June 22, 1953. In this application it is proposed to use as a binder one which is compatible with the components of the sensitizing solution so that the silica and binder may be added thereto. While this did away with the extra coating step of Sulich and Frederick it, nevertheless, had the other drawbacks of their procedure enumerated above. Therefore, while this system was closer to the mark it did not contribute that for which the industry has been seeking for so many years.

It has now been discovered, and most unexpectedly so, that the problem which has so long been a thorn in the side of the industry is completely solved, and without resort to binders or other contaminates, by dispersing in the aqueous sensitizing solution an almost chemically pure silica produced by a high temperature gas phase decomposition and composed of extremely fine-sized, well-defined particles, and then coating the resulting dispersion on a suitable base.

The manufacture of diazotype materials in this fashion, said diazotype materials and the processing thereof constitute the purposes and objects of the present invention.

The silica, the use of which is contemplated herein, is free from iron, is essentially 99% silicon dioxide and has a particle size ranging from .015 to .020 micron. Said silica is manufactured by a high temperature decomposition of a siliceous material in a gaseous medium which insures spontaneous formation of the silica in said medium. Various methods have been worked out for securing this result. One such method involves the burning of a siliceous material, such as silicon tetrachloride in an atmosphere of hydrogen to effect very rapid formation of the silicon dioxide in a small particle size in a gaseous atmosphere. The same result may be effected while utilizing ethyl silicate as the parent material and air as the gaseous atmosphere. Silica made in this fashion is available from G. L. Cabot, Inc., Boston, Massachusetts, under the trademark "Aerosil."

Another method involves dissolution of a silicate in a solvent, the application of heat and pressure and the sudden release of the pressure to effect spontaneous formation of the silica in a gaseous medium. More specifically, this method involves adding dilute sodium silicate to dilute sulfuric acid, adjusting the pH and allowing a gel to form. The gel is then leached free from sodium sulfate with water and the water replaced with alcohol. The alcohol saturated gel is placed in an autoclave and heated until the critical temperature and pressure are reached.

The alcohol is then removed by relieving the pressure and applying a vacuum. Under these conditions, there is no shrinkage of the gel as there would be in a normal drying process. Silica manufactured in this fashion is available from Monsanto Chemical Company, St. Louis, Missouri, under the trademark "Santocel."

The silica is easily added to the sensitizing composition in the form of a dry powder. It is then dispersed by high speed agitation or the like until the resulting composition is homogeneous. Conversely, the silica may be dispersed separately by slurrying with water or with a small portion of the sensitizing composition to produce a thin, uniformly homogeneous paste which is then added to the slurry of the sensitizing composition with stirring.

The quantity of the silica which is added amounts to about .5 to 10% by weight of the sensitizing composition. Best results, however, are obtained when the silica is present in a concentration of 2.5% to 6% by weight of the sensitizing solution.

The sensitizing solution is applied to the base material by any convenient means, as for instance, roller application, spraying, brush coating or the like. Care must be taken, however, to insure that the excess is doctored off, either with an air knife, doctor blade or similar means.

In the preparation of the sensitizing solutions, I may use any of the customary light sensitive diazonium compounds, and, in this connection, reference is made to the compounds referred to in U. S. P. 2,501,874 and in the article by Van der Grinten, Photographic Journal, vol. 92B, 1952, page 46. The stabilized diazos derived from N,N-disubstituted p-phenylenediamines are most satisfactory. Examples of such diazos are those derived from N,N - diethyl - p - phenylenediamine; N - benzyl - N-ethyl - p - phenylenediamine; N - ethyl - p - phenylenediamine; N - phenyl - p - phenylenediamine; N,N - diethyl-2 - ethoxy - p - phenylenediamine; N - ethyl - 2 - methyl-p - phenylenediamine; N,N - bis(β - hydroxyethyl) - p-phenylenediamine; N-β-hydroxyethyl-N-methyl-p-phenylenediamine and the like. According to customary procedure these diazos are used in the form of salts stabilized with zinc chloride, tin chloride, cadmium chloride and the like.

The comments with regard to the diazonium compounds apply equally to the coupling components. Thus, any of the usual coupling components are satisfactory for my purpose. Examples of such couplers are 2,3-dihydroxynaphthalene; 1,8-dihydroxynaphthalene; resorcinol, octyl resorcinol; p-methyl-N-phenylpyrazolone; the amide of α-resorcylic acid; 2-hydroxynaphthalene-3,6-disulfonic acid; 2,5-xylenol; H acid; acetyl acetanilide; 2,3-dihydroxynaphthalene-6-sulfonic acid and the like. Other couplers are mentioned in the Van der Grinten article supra.

The coating solution may also contain the various adjuncts usual in the manufacture of light sensitive diazotype materials. These include metal salts for intensification of the dyestuff image, such as ammonium sulfate, nickel sulfate, zinc chloride and the like; stabilizing agents such as thiourea, thiosinamine; naphthalene trisulfonic acid and the like; acids acting to retard precoupling such as acetic acid, boric acid, tartaric acid and the like; hygroscopic agents such as glycol, glycerin and the like; and wetting agents such as saponin, lauryl sulfonate, keryl benzene sulfonate, the oleic acid amide of N-methyl taurine and the like.

The base to which the coating solution is applied may be any of those which have been previously suggested for employment in the diazotype field. Examples of such bases are high grade all-sulfite paper, rag paper, rayon or cotton cloth, starch filled cloth, partially hydrolyzed cellulose acetate filmbase, regenerated cellulose acetate and the like.

The pigment contemplated for use herein has many important attributes, some of which are explainable and others of which are inexplicable. Thus, since the pigment is prepared in the gaseous phase, it is easily dispersed due to the high degree of particle separation and once properly dispersed remains suspended in the sensitizing solutions without the necessity of agitating or circulating systems which must be employed with silica of larger particle size. Furthermore, because of the gas phase preparation the silica does not come into contact with metallic processing equipment, and as a consequence is almost completely free from contamination with iron, an element which is extremely detrimental in diazotype materials.

Colloidal silica, however, formed in the liquid phase and employed according to Jahoda and von Glahn and Stanley is highly contaminated with iron.

Prints made while utilizing said silica have greatly improved dye density and brightness as compared with prints made according to the process of Jahoda and von Glahn and Stanley. Such prints, moreover, have a desirable matte appearance possessing excellent pencil tooth in contrast to the glossy image characteristic of prints obtained

according to the prior art while using colloidal silica. Prints produced with the silica described herein, moreover, are free from feathering to ink line. Feathering is a common characteristic of prints made while utilizing the colloidal silica of the prior art.

One of the most outstanding advantages of sensitizing compositions containing the silica contemplated herein is the possibility of extending diazotype coatings to very desirable bases which heretofore could not be so employed. The inability of the art to use such bases was attributable to a tendency of the bases to repel the coating compositions, for one reason or another, such as supercalendering of the surface, impregnation of the base with hydrophobic materials and the like. In any case, the coating of such papers in the past led to little success and in many instances the coating compositions were shed by the surfaces involved to an extent equivalent to the shedding of water by the proverbial duck's back. Bases of the type which I have in mind are, for example, of highly calendered 100% rag paper, particularly when transparentized by use of resinous materials, waterproof tracing paper, tracing cloth calendered with hydrophobic lubricants and the like. Despite the fact that there has been a marked demand for diazotype materials in which such materials operate as a base, due to the inability of the art to uniformly coat such bases without obtaining a mottled effect, they have been rarely used.

It has now been found, however, that the coating compositions containing the silica previously mentioned eliminate the tendency of the bases to repel the coating compositions and to do away with the non-uniform coatings previously obtained. The particular reason why said colloidal silica operates as it does with these particular surfaces is not known and has not been completely investigated. Conceivably, the phenomenon mentioned is bottomed on a surface abrasion by the silica particles which renders the surface sufficiently matte in finish so that a smooth coating may be obtained. In any event, regardless of the theory, the fact is that by employing the aforesaid silica, it is possible to use papers of hydrophobic nature which heretofore had been considered of no utility in this field because of their resistance to uniform coatings. Manifestly, this extension of the diazotype coating technique to extremely desirable bases is a matter of great magnitude from the standpoint of the customer and manufacturer.

It has been pointed out that the silica used herein has a particle size ranging from .015 to .020 micron, i. e., it is within the colloidal range. The marked differences in result obtained when using said silica appear to be attributable to some indeterminate physical change which takes place when the silica is laid down with the sensitizing solution. It is my opinion that this physical change involves an agglomeration of the silica particles to a size beyond the colloidal range. Such modification would explain the difference in appearance of the prints obtained according to the prior art, on the one hand, and according to my method, on the other hand. However, if agglomeration is the true answer, then the effect is surprising since it has been previously stated that the silica hereof is easily dispersed and when properly dispersed remains in suspension. It was, therefore, to be expected that having this property the silica would be laid down in the form of a film of discrete particles as in Jahoda and von Glahn and Stanley. Despite the theory involved, however, it is a fact that when using the silica contemplated by me, results are obtained which are so outstanding as to leave no comparison with the prior art procedures. It might be emphasized too, in this connection, that binders are completely unnecessary and even with their elimination no crocking takes place as it does when particles outside the colloidal range are employed.

The following examples will serve to illustrate the invention, but it is to be understood that the invention is not restricted thereto.

Example I

A sensitizing solution for black line prints was prepared from the following components:

Water	cc.	70
Ethylene glycol	cc.	5
Alcohol	cc.	1
Citric acid	grams	5
Zinc chloride	do	5
Thiourea	do	5
Resorcinol	do	0.5
Acetoacetanilide	do	0.1
2,7-dihydroxynaphthalene-3,6-disodium sulfonate	do	3.8
p-Diethylamino benzene diazonium chloride, zinc chloride double salt	grams	3
Saponin	do	0.1

Water to make 100 cc.

Three grams of finely divided silica of the type previously described was dispersed in the resulting solution by passing the silica in solution through a mixer and then, if desired, through a colloidal mill to break up any agglomerates.

The sensitizing solution was coated on high-grade all sulfite bond paper and dried. The prints made from these coatings had a matte rather than a glossy effect and showed considerable enhancement in density when compared to prints made with the same sensitizing ingredients while employing silica of colloidal or of larger particle size according to prior methods described above.

There was no tendency, moreover, for the silica pigment to rub off the prints.

Example II

High-grade all sulfite bond paper is coated with a sensitizing solution of the following composition:

Water	cc.	70
Ethylene glycol	cc.	5
Alcohol	cc.	2
Citric acid	grams	5
Thiourea	do	5
Zinc chloride	do	5
2,3-dihydroxynaphthalene-6-sulfonic acid	do	3
p-Diazo-N-diethyl aniline	do	2
Saponin	do	0.1
Fine sized silica	do	3

Water to make 100 cc.

in which the silica, having the characteristics previously stated, is dispersed in the sensitizing solution as in Example I.

The blue line prints obtained from the coatings of this example have characteristics similar to those of Example I.

Example III

A high-grade well-sized bond paper is coated with the following sensitizing solution:

Water	cc.	80
Ethylene glycol	cc.	7
Citric acid	grams	5
Boric acid	do	2.5
Thiourea	do	5
Zinc chloride	do	5
Resorcinol	do	2
p-Diazo(N-hydroxyethyl-N-methylamino)aniline	grams	4
Saponin	do	0.1
Fine sized silica	do	2.5

Water to make 100 cc.

The silica of the type previously described is dispersed in the solution according to Example I. The sepia line

prints formed according to this example have the characteristics noted in connection with the prints of Examples I and II.

Various modifications of the invention will occur to persons skilled in the art, and I, therefore, do not intend to be limited in the patent granted except as necssitated by the appended claims.

I claim:

1. Sensitizing compositions for light sensitive diazotype materials comprising an aqueous dispersion of a light sensitized diazonium compound, an azo dye coupling component and a silica free from iron having a particle size ranging from .015 to 0.20 micron, and obtained by rapid high temperature decomposition of a siliceous material in a gaseous medium.

2. The composition as defined in claim 1, wherein the silica is present in an amount ranging from about .5 to 10% by weight of the sensitizing solution.

3. The composition as defined in claim 1, wherein the silica is present in an amount ranging from about 2.5% to 6% by weight of the sensitizing solution.

4. Light sensitive diazotype materials comprising a base impregnated with the sensitizing composition of claim 1.

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