The present invention pertains to light sensitive diazo-type materials having fast printing speed and being capable of yielding images of high density, and more particularly to such materials in which the light sensitive component is located on the base in a layer comprising a polyvinyl ester having finely divided alumina dispersed therethrough. It has become customary with users of the diazo-type process and sensitized materials thereby to demand faster printing materials which, at the same time, yield images of higher density upon a clean white background. Inasmuch as the diazo process in commercial use is a bleach-out, positive process it is manifest that problems are encountered in meeting these demands. If, for example, one uses a given diazo of a certain wavelength, light sensitivity it is obvious that a reduction in concentration of the diazo will permit one to achieve faster printing speed. This is, of course, attributable to the fact that one need burn out less diazo in order to obtain the image. It is equally evident, however, that the increase in printing speed is only obtained by a sacrifice in the azo dye density of the image produced by development. Meeting the requirements of the art is, therefore, not as simple as it appears.

The difficulties involved have been recognized and have been grappled with by those in the industry. Several shrewd approaches to a solution have been made, certain of which have achieved great success and others of which have been of little moment. Despite the progress which has been made the art is a long way from providing a product of optimum characteristics.

The most obvious approach to the problem involved is the selection of a diazonium compound having such a high light sensitivity that it may be used in a concentration which will give the required image density while still permitting complete burn-out in the “whites” in the desired period of time. To this end, numerous diazos of widely varying chemical structures have been proposed, synthesized and tested in the diazo-type process. Of these compounds the stabilized diazov derived from N,N-disubstituted p-phenylenediamines appear to offer the best compromise between high light sensitivity and greater dye density, on the one hand, and the other requisite features such as water solubility in coating solutions, stability to decomposition and/or precoupling, fastness properties and the like, on the other hand.

Another tack has been the use of additives in the diazo-type coating solution to increase the burn-out sensitivity of the diazo in the light struck areas. For this purpose there has been proposed such compounds as anthraquinone diazonium acid, ketonic organic compounds and the like. It is evident that this phenomenon, if successful, would permit more diazo to be used in the sensitized layer and thereby result in a higher density in the image areas with no sacrifice in printing speed. Unfortunately, this approach has met with but limited success, the result not being commercially satisfactory on a quality or cost basis.

A further approach has been to utilize the image surface more efficiently by the application of a more or less discontinuous layer of a chemically-inert, but physically-active, finely divided material such as finely divided silica. In this procedure it has been suggested that such layer be applied by pretreatment of the base or that it be layered down from the coating solution. Thus, U. S. P. 2,435,515 (Reissue 23,510) suggests the formation of a diazo-siliceous layer from a colloidal liquid dispersion of silica as a pretreatment for paper, which is then sensitized with a blue print solution. It is claimed that the brightness and density in the resulting print are thereby enhanced. Conversely, U. S. P. 2,657,709 proposes to produce the same improvement in the diazo-type system of photoreproduction by the incorporation of colloidal silica in a dispersed state in a diazo sensitizing solution. The latter procedure has the very important added economic advantage of eliminating a separate coating step.

It has been found in practice, however, that these two procedures possess certain disadvantages, the gravest of which are (1) rub-off; (2) the action of the silica layer as a chromatographic separator, and (3) cost.

Rub-off, or powdering-off, as the name implies involves the tendency of the silica particles to be removed during manufacture and end use of the diazo-type materials. This action is not only very annoying but in addition may present potential health hazards.

It has been ascertained also that the silica layer acts as a chromatographic separator toward the several ingredients present in a typical diazo coating solution. This results in poorer stability, poorer fade resistance, and, in the case of the black line (which uses a multiplicity of coupling components) off-colored blacks.

It has been stated that the use of the silica layers in the above patents enhanced brightness and density. It is to be noted, however, that the degree of improvement when weighed against the aforesaid objections, the increased cost and extra efforts in disappointing results, U. S. P. 2,662,013, issued December 8, 1953, it is suggested that the above disadvantages be eliminated by the use of binding agents for the silica particles. As such binding agents it is proposed to use those containing chemically bound nitrogen, either in the form of naturally-occurring proteinaceous materials or synthetic resins. It was discovered that the proper ratio, experimentally-determined, of silica to binder was of critical importance. In fact, it was found that at the proper ratio of silica and binder, a synergistic effect took place, viz., density enhancement was out of all proportion to that obtained when either component was used, or when the two were used together at concentrations other than the optimum. Further studies revealed that silica particles of 1 to 5 micron size gave appreciably greater density enhancement than the smaller particles recommended in the aforesaid patents. However, particles above 10 micron size were avoided since they were difficult to maintain in suspension in the precoating bath and produced undesirable surface roughness in the dried coating.

The procedure of the above patent was a marked commercial advance. However, it had one drawback, this being the incompatibility of the suggested binders with the requisite ingredients of the sensitizing solution. As a consequence, it is necessary in coating according to the above patent to apply the silica-binder dispersion in a separate precoating operation. The use of two coating operations, coupled with the extra handling of the materials involved, manifestly increases the production costs.

We finally discovered that the advantages of the above
procedure could be obtained while avoiding the additional coating step by using alumina in lieu of silica and, as
the binder for the alumina, a water insoluble polystyrene ester compatible with the ingredients of the sensitizing
solution. Sensitizing solutions containing a polystyrene ester as the binder, along with finely divided alumina, light
sensitive diazo type materials prepared from such compositions, and the processing of such diazo type materials
therefore, constitute the purposes and objects of the present
invention.

The water insoluble polymers, the use of which is con-
templated herein, may be a polystyrene ester per se, such as
polystyryl acetate, polystyryl chloride or the like, or
copolymers of a vinyl ester, such as vinyl chloride, vinyl
acetate or the like, with another vinyl compound copoly-
merizable with such ester, i.e., acrylic acid, styrene or the
like. The vinyl ester in such copolymers will range from
10 to 40 parts by weight. These polymers and copoly-
mers are employed in the form of aqueous dispersions in
which the solids content is 40 to 50% by weight. Such
copolymers are readily obtainable in the open market.

Our experiments to date indicate that the polystyrene
esters in such dispersions, in order to be effective, must
possess either a cationic charge or must possess no charge,
i.e., be non-ionic. If the polystyrene ester carries an
anionic charge it is incompatible with the coupler of the
sensitizing solution causing premature precipitation ther-
of. The use of such polymers must be avoided at all cost.
Polystyrene esters containing a cationic charge produce best
and are, therefore, recommended for use.

The alumina which we use in our dispersions may be
either colloidal in character or may be of a coarser grade,
i.e., ranging from 1 to 5 microns in size. We find that we
can obtain best results with the coarser particles and so prefer
their use.

Any of the usual light sensitive diazonium compounds
may be employed and, in this connection, reference is
made to the compounds referred to in U.S. Pat. 2,501,874,
and in the article by Van der Grinten, Photographic
acids derived from N,N-disubstituted p-phenylenediamines
are most satisfactory. Examples of such diazo acids are those
derived from N,N-diethyl-p-phenylenediamine; N-benzyl-
N-ethyl-p-phenylenediamine; N-ethyl-p-phenylenediamine;
N,N-diethyl-2-ethoxy-p-
phenylenediamine; N,N-diethyl-2-methyl-p-
phenylenediamine; N,N- bis(4-hydroxyethyl)-p-phenylenediamine; N,N-4-
hydroxyethyl-N-methyl-p-phenylenediamine and the like.
According to customary procedure these diazo acids are used in
the form of salts stabilized with zinc chloride, tin chloride, cadmium chloride and the like.

The coatings are applied either by the diazonium compounds apply equally to the coupling components. Thus,
any of the usual coupling components are satisfactory for
our purpose. Examples of such couplers are 2,5-xyleneol;
2,3-dihydroxynaphthalene; 1,8-dihydroxynaphthalene; resi-
ordine; octyl resorcinal; p-phenyldiamine-pyrazolone;
the amide of acetic acid; 2-hydroxynaphthalene-3,6-
disulfonic acid; H acid; acetyl acetanilide; 2,3-dihydroxy-
benzenesulfonic acid and the like. Other couplers are
mentioned in the Van der Grinten article supra.

The coating solutions, in addition to the polymer, alumina
and light sensitive diazo dye may contain the various ad-
juvants usual in the manufacture of light sensitive diazo
type materials. These include metal salts for intensifi-
cation of the dye stuff image, such as ammonium sulfate,
nickel sulfate, zinc chloride and the like; stabilizing agents
such as thioaurea, thioisourea, naphthalene sulfonic acid and the like; acids acting to retard precoupling such as
acetic acid, boric acid, tartaric acid and the like; hy-
groscopic agents such as glycerol, glycine and the like; and
wetting agents such as saponin, laurel sulfonate, ketyl
benzene sulfonate, the oleic acid amide of N-methyl
taurine and the like.

It is also recommended that agents be used which have
the property of accelerating the rate of azo dye color
development, particularly under conditions of low ammonia concentration. For this purpose there are used
thioaurea derivatives and particularly those in which either
one or both nitrogen atoms are substituted by an aromatic
radical. Examples of such compounds are 1-allyl-3-9-
hydroxystyryl-2-thioura; 1-allyl-2-thiouria and the like.
The ratio of alumina to binder is not as critical as in our
procedure as in the procedure of U.S. Pat. 2,662,013.
Thus, the quantity of binder may range from 5% to 1
part by weight for each part by weight of alumina. The
quantity of alumina, on the other hand, based on the weight
of the light sensitive diazonium compound is about
1 part of the diazonium compound to 1 to 4 parts of
alumina.

The base to which our coating solution is applied may
be any of the bases which have been previously sug-
gested for use in the diazotype field. Examples of such
bases are high grade all-sulfite bond paper, rayon or cot-
ton cloth, starch filled cloth, partially hydrolyzed cellu-
lose acetate filmbase, regenerated cellulose acetate
and the like.

One of the particular advantages of our development is
the fact that it may be used not only with the dry devel-
opment process, but also with the one component moist
process. It is recommended that when the latter proce-
sure is employed, a small amount of a fluoride be added
to improve the solubility of the diazo in the coating
solution. For this purpose there may be employed am-
nium bifluoride, sodium fluoride, potassium fluoride and
the like. Generally, these salts are added in an
amount ranging from .5 to 4 grams per hundred cc. of
coating solution.

Our procedure is carried into effect by dissolving in
water the various components of the sensitizing solution
and then dispersing therein the desired quantity of alu-
mina and polymer. Any of the apparatus usual for the
formation of dispersions may be employed. The base is
then coated with the suspension, dried and processed
either by the dry or wet method, depending upon whether
the coating solution is a two or one component solu-
tion.

Our interpretation of the action by which we are able to
obtain our results is as follows:

The polystyrene ester dispersion is essentially composed of
discrete water insoluble particles of resin with tiny
amounts of polystyrene alcohol in solution. Being in
the insoluble state, the concentration used raises viscosity
negligibly compared to what a typical water soluble resin
in an equally effective concentration would. This
permits rapid sensitizing and drying during the coating
operation. The low pH of the coating solution in combi-
nation with the heating applied during the drying step
hydrolyzes a small amount of the polystyrene ester to poly-
vinyl alcohol on the surface of the particles thus making
these particles more receptive to impregnation by the
coating solution ingredients. Furthermore, the low block
temperature of the resin permits a portion of the particles
to fuse during the drying step. This fusion, together with
the well-known adhesive qualities of the polystyrene ester,
makes its binding properties upon the silica especially de-
sirable. In the diazotype system in which this polysty-
rene ester is used, one can thus visualize the effects of coating
solution and resin acting upon one another to produce
in a discrete particle, discontinuous film form, a mixture
of polystyrene alcohol and polystyrene ester, the latter being
partially hydrolyzed, unhydrolyzed and partially fused.
This mixture represents a very effective manner for re-
cieving the coating solution and enhancing the density of
the dye images formed therein.

The invention will be more fully understood from the
following examples which are illustrative only. The parts
are by weight unless otherwise stated.
Example I

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

Water .......................................................... cc... 60
Ethylene glycol or glycerin ....................................... cc... 5
Isopropyl alcohol ................................................. cc... 1
Citric acid ......................................................... grams... 5
Zinc chloride ....................................................... do... 5
N-γ-hydroxyethyl-N'-allyl-thiourea ............................... do... 2.5
2,3-dihydroxy naphthalene-6-sulfonic acid .................... do... 4
4-N,N-diethylamino benzene diazonium chloride.............. do... 3
Finely divided alumina of 1–5 micron size ................... do... 6
50% solids cationic type polyvinyl acetate aqueous suspension ................................................. cc... 0.1
Saponin .................................................................. grams... 0.1
Water to .................................................................. cc... 100

and then dried. Prints were made and developed in an aqueous solution composed of:

Water .......................................................... cc... 100
Sodium carbonate ................................................... grams... 2
Sodium thiosulfate .................................................. do... 5
Thiourea .............................................................. do... 2.5
Tertiary sodium phosphate ......................................... do... 0.5
Sodium chloride ..................................................... do... 4
Phloroglucinol ....................................................... do... 1
Resorcino1 ............................................................ do... 0.5

When these were compared to similarly made prints whose coatings were from a solution not containing the proposed additives, the former were considerably superior in density.

Example II

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

Water .......................................................... cc... 60
Ethylene glycol or glycerin ....................................... cc... 5
Isopropyl alcohol ................................................. cc... 1
Citric acid ......................................................... grams... 10
Zinc chloride ....................................................... do... 5
N-γ-hydroxyethyl-N'-allyl-thiourea ............................... do... 2.5
Diresorcy! sulfoxide .............................................. do... 1.3
Acetoacetanilide .................................................. do... 0.07
2,3-dihydroxy naphthalene-6-sulfonic acid .................... do... 1.9
4-N,N-diethylamino benzene diazonium chloride.............. do... 3
Finely divided alumina of 1–5 micron size ................. do... 6
50% solids cationic type polyvinyl acetate aqueous dispersion ................................................. cc... 0.01
Saponin .................................................................. grams... 0.1
Water to .................................................................. cc... 100

and then dried. Prints were made and compared in a fashion analogous to those in Example I reveal the same improvements.

Example III

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

Water .......................................................... cc... 60
Aluminum sulfate ................................................. grams... 1.5
Thiourea .............................................................. do... 0.5
Citric acid ......................................................... do... 0.5
Ammonium bisulfite .............................................. do... 0.75
4-N-benzyl-N-ethyl benzene diazonium chloride .......... do... 3
Finely divided alumina of 1–5 micron size ................. do... 6
50% solids cationic type polyvinyl acetate aqueous dispersion ................................................. cc... 3
Water to .................................................................. cc... 100

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