Patented June 12, 1945 2,378,276

# UNITED STATES PATENT OFFICE

2,378,276

## STABILIZATION OF COLORING COMPOSITIONS, CONTAINING DIAZONIUM SALTS

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No Drawing. Application July 5, 1943, Serial No. 493,593

9 Claims. (Cl. 8—71)

This invention relates to compositions containing diazonium salts derived from ice color diazo components and to methods of preventing the thinning of printing pastes containing such diazo compounds.

An important method of producing prints of azoic colors on vegetable fibers consists in padding the goods with an alkaline solution of an azoic coupling component and printing these goods with a printing paste containing a diazonium salt derived from an ice color diazo component. The diazonium salt is either prepared by the printer himself by diazotizing the corresponding base or it is applied in the form of a stable diazonium salt. This simple and well known cheap process is open to a very serious disadvantage. The printing pastes containing the diazonium salts and a carbohydrate thickener tend to thin out rapidly losing their desired printing consistency. It is with this thinning action that the present invention is concerned.

According to the present invention the diazonium salt is associated with a water soluble ester of a di-basic or tri-basic organic carboxylic or sulfonic or sulfocarboxylic acid, the alcoholic component of the ester containing at least one olefinic double bond or acetylenic triple bond for each 12 carbon atoms of the ester.

When an aromatic amine is diazotized in acid solution, a diazonium salt is formed which is generally assumed to have the following formula:

$$ArN^{+}\ X^{-}$$
$$\|$$
$$N$$

where Ar stands for the aromatic radical of the diazo component and X stands for the anion of the acid. These diazonium salts are salts of the very strong diazonium bases and the aqueous solutions contain essentially the diazonium cations and the anions of the acid used, as indicated by the formula. Some of these diazonium salts are difficult to isolate because of their great solubility. Others are not so soluble and can be easily isolated. Some are difficult to handle after isolation because of their explosivity, others are rather stable and do not represent an explosive hazard. It is also known that if the anion of the acid $X^-$ is properly chosen, in almost all cases diazonium salts of lower solubility may be produced and therefore isolated, and it is also known that many of these diazonium salts have lost their explosive character and can be stored and handled in the dry state without danger; this kind of diazonium salt is sometimes referred to as "stabilized" diazonium salts. They comprise such compounds as certain aromatic sulfonates, without olefinic double bonds, borofluorides, and particularly salts of complex acids sometimes referred to as double salts, the most important of them being the double salts of diazonium chlorides and zinc chloride which correspond to the formula:

$$\left(\begin{matrix}ArN\\ \|\\ N\end{matrix}\right)_2^{++}\ (ZnCl_4)^{=}$$

It should be borne in mind that also these "stabilized" diazonium salts including the above mentioned double salts are true diazonium salts, i. e. the aqueous solution contains the same diazonium cations as the solution of any other diazonium salt derived from the same base.

The stabilized diazonium salts should not be confused with other kinds of stabilized diazo compounds such as diazotates, also known as nitrosamines, or diazoamino and diazoimino compounds which are only stable and applied in alkaline medium, while on the other hand the diazonium salts are only stable and applied in acid medium. The present invention deals with inhibiting the thinning action of diazonium salts only and not with any similar action that might be observed with other types of diazo compounds. Whenever stabilized diazo compounds are referred to in this application this term shall be interpreted to include exclusively stabilized diazonium salts and not to include diazotates or diazoamino or diazoimino compounds.

While it is not intended to limit the present invention to any theory of action, we believe that it is highly probable that lowering of viscosity of printing gums is essentially caused by the diazonium cation because the same kind of thing results regardless of the anion of the diazonium salt and even the double salts of the stabilized

diazonium salts described above exert a similar thinning action. Presumably in aqueous solution the stabilized diazonium salts are ionized to give the same diazonium cation. The pH of the printing paste is not critical so long as it is on the acid side for the present invention does not deal with any other types of pastes. Alkaline media, as is well known, cause rearrangement of the diazonium salts to diazo compounds of different structure which are referred to as diazotates or nitrosamines.

While not desiring to limit the invention thereto, we believe that the evidence strongly indicates that the thinning action is a colloidal phenomenon rather than a chemical reaction. The following test was made:

A diazonium salt derived from 2-nitro-4-methoxy aniline was added to a printing paste made up with a starch thickener; after 20 hours the then water thin solution was coupled with an alkaline solution of betanaphthol and the azo dye formed was removed by filtration. The amount of azo dyestuff obtained indicated that the bulk of the diazonium salt was undecomposed and had reacted while the filtrate still showed the reaction of starch and not the reactions of reducing sugars.

The thinning action differs widely and depends upon the structure of the diazo component the diazonium salt derives from. We have found that those diazonium salts that are known to be very active couplers are also the worst thinners, while those that are slow in coupling generally thin to a much lesser degree. Though there is certainly some parallelism in the coupling power and thinning action, these two properties are not strictly proportionate. The diazonium salts that derive from nitroanilines are the worst thinners. Particularly those derived from 2,4-dinitro-6-chloroaniline, from 2-nitro-4-chloroaniline, from 2-nitro-4-methoxy aniline, from 2-nitro-4-methylaniline thin the vegetable gums very badly. The diazonium salts deriving from o-nitraniline thin more than those deriving from the meta and para compound. On the other hand the diazonium salts derived from 2-methyl-4-chloroaniline and from o-anisidine have only little thinning action. Obviously the rate of the thinning depends upon the concentration of the diazonium ions present in the printing paste.

The thinning action has been observed with all thickeners prepared from materials of vegetable origin such as starches, gums, alkyl celluloses, etc. Wheat starch, corn starch, rice starch, sweet potato starch, tapioca starch and chlorinated starch may be mentioned as examples of starches. Carob bean gum and gum tragacanth may be mentioned as examples of gums and methyl- or ethyl-cellulose as examples of alkyl cellulose. Obviously, also mixtures of these materials are quite often used in thickeners and their viscosity is equally influenced by diazonium salts. It will be noted that all of the thickeners are carbohydrates or carbohydrate derivatives. In the claims the expression "carbohydrate thickener" is used in a broad sense to cover pure carbohydrate derivatives.

We have found that the water soluble esters of di- and tri-basic organic carboxylic, sulfonic or sulfocarboxylic acids delay the thinning provided there is present at least one olefinic double bond or acetylenic triple bond for each 12 carbon atoms of the ester. The thinning effect can be reduced to the point where it becomes harmless from the practical point of view. While it is not intended to limit the present invention to any theory of action of the inhibitors, the following hypothetical explanation is offered as being probable without intending to restrict the invention thereto.

We believe that the diazonium cations which are the active thinning agents are unsaturated and have a marked tendency to combine. This unsaturated character is probably responsible for the ease with which they combine with coupling components to form azo dyestuffs. When an unsaturated thinning inhibitor, such as a water soluble ester of di- and tri-basic organic carboxylic, sulfonic or sulfocarboxylic acids is added to the diazonium salt solution before the printing thickener is added, it is probable that the diazonium cation forms a loose complex with the thinning inhibitor which decreases the affinity of the diazonium cation and inhibits its action upon the thickener. When the thickener is first added to the diazonium salt solution followed by addition of the thinning inhibitor, thinning is prevented to a much lesser degree. Apparently in such case the diazonium salt has already commenced its thinning action on the thickener and the action is not reversible so that the addition of the thinning inhibitor does not remedy the damage already done.

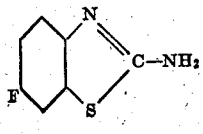
The present invention includes all the diazonium salts derived from ice color diazo components, that is to say, for all diazotizable aromatic amines free from solubilizing groups useful in making ice colors or azoic pigments. Typical are the following:

Aniline and its homologues, as e. g. the toluidines, 2,4-dimethylaniline; halogen derivatives of aniline and of its homologues, as e. g., the monofluoroanilines, the monochloranilines, 2,5-difluoroaniline, 2-fluoro-5-chloroaniline, 2,5-dichloroaniline, m-aminobenzotrifluoride, p-aminobenzotrifluoride, 3-amino-4-chlorobenzotrifluoride, 2-methyl-3-chloroaniline, 2-methyl-4-chloroaniline, 2-methyl-5-chloroaniline, 3-methyl-4-chloroaniline, 5-methyl-2-chloroaniline, 2-methyl-4-chloro-5-bromoaniline, 2-methyl-4,5-dichloroaniline, 4-methyl-2,5-dichloroaniline; nitro derivatives of aniline and of its homologues and their halogen derivatives, as e. g. the nitroanilines, 2-methyl-4-nitroaniline, 2-methyl-5-nitroaniline, 4-methyl-2-nitroaniline, 2-nitro-4-fluoroaniline, 2-nitro-4-chloroaniline, 3-nitro-4-chloroaniline, 4-nitro-2-chloroaniline; ether derivatives of primary aromatic amines and their halogen derivatives, as e. g. o-anisidine, 2-methoxy-5-methyl aniline, 2,5-dimethoxy-aniline, 2-methoxy-1-naphthylamine, 2-amino-diphenylether, 2-amino-4-acetyl-diphenylether, benzyl-2-aminophenyl-ether, 3-fluoro-4-methoxyaniline, 2-methoxy-5-chloroaniline, 2,5-dimethoxy-4-chloroaniline, 2-methoxy-4-chloro-5-methylaniline, 2-methoxy-5-bromoaniline, 3-bromo-6-ethoxy-aniline, 4-chloro-2-amino-diphenylether, 4-amino-2-chloro-diphenylether, 4-amino-4'-chloro-diphenylether, 4,4'-dichlor-2-aminodiphenylether, 2,2',5'-trichloro 4-amino-diphenylether; ether derivatives of aniline and its homologues containing nitro groups as e. g. 2-methoxy-4-nitroaniline, 2-methoxy-5-nitroaniline, 2-nitro-4-methoxy-aniline, 2-methoxy-4-nitro-5-methyl-aniline; monoacyl derivatives of aromatic diamines, as e. g. N-hexahydrobenzoyl-p-phenylene diamine, N-hexahydrobenzoyl-p-toluylene diamine, N-benzoyl-p-phenylene diamine; monoacyl derivatives of diamino-phenol ethers as e. g. 2-benzoylamino-4-aminoanisole, 2-hexahydrobenzoylamino-5-

aminoanisole, 2-amino - 5 - benzoylamino-hydroquinone dimethylether and diethylether, 2-amino-5-hexahydrobenzoylamino-hydroquinone dimethylether and diethylether, 2-amino-5-butyrylamino-hydroquinone dimethylether and diethylether, 2-amino-5 - penoxyacetylamino - hydroquinone diethylether, the monomethyl and the monobenzyl and the monophenyl-urethane of 2,5-diamino-hydroquinone dimethylether and diethylether, 1-amino-3-benzoylamino-4,6-dimethoxy-benzene; analogous monoacyl derivatives of 2,5-diamino - 4 - alkoxy - toluenes and of 2,5-diamino-4-alkoxy-chlorobenzenes and of 2,5-diamino-4-alkoxy-benzene sulfodialkylamides; analogous monoacyl derivatives of 1,3-diamino-4,6-dimethylbenzene; the diethylamide of 2-amino-4(4'-chlorophenoxy)-benzoic acid; monoacyl derivatives of diamino-p-chlorophenyl ethers as e. g. 2-amino-4-chloro-5-acetylamino - diphenylether, 2-benzoylamino-4-chloro-5-aminoanisole; amino derivatives of aromatic sulfones as e. g. 3-amino-4-methyl-diphenyl sulfone, 2-amino-4'-methyl-diphenyl sulfone, 2-amino-4-acetyl-diphenyl sulfone, the ethyl ester of 3-amino-4-(p-toluene-sulfonyl)-benzoic acid, 4 - methoxy-3-amino - phenyl-ethyl sulfone, (4-methoxy-3-amino-phenyl) - benzyl sulfone, 4-ethoxy-3-amino-diphenyl sulfone, 2-amino-4-(trifluoromethyl)-phenyl-ethyl sulfone; amino derivatives of aromatic dialkylsulfonamides as e. g. 3-amino-4-methyl-benzene dimethylsulfonamide and diethylsulfonamide, 3-amino-4-methoxy-benzene diethylsulfonamide; xenylamine; alpha and beta naphthylamine; alpha amino anthraquinone; 2-amino-3-nitro-fluorene and 2-amino-3-nitro-fluorenone; amino-diarylamines and their ether derivatives and their nitro derivatives as e. g. 2-methoxy-5-amino-diphenylamine, 4-methoxy-4'-amino-diphenylamine, 4 - ethoxy-4'-amino - diphenylamine, 3,4'-dinitro - 4-amino - diphenylamine; amino-azo compounds, as e. g. 3,2'-dimethyl-4-amino-azobenzene, 2-methyl-4-amino-5-methoxy-4'-chloro - azobenzene, 4-amino-4'-nitro-3-methoxy-6-methyl-azobenzene, 4-amino-4'-nitro-2,5-dimethoxy-azobenzene, 4-amino-4'-chloro-3-methoxy-6-methyl-azobenzene, the azo dye: diazotized o-anisidine coupled onto alpha naphthylamine.

There are also diazonium salts derived from aromatic diamines in which only one of the amino groups is diazotized and they also fall within the scope of the present invention. An example of this type of amine is 2,5-dichloro-1,4-phenylene diamine. Diazonium salts derived from diamines in which both amino groups are diazotized to form tetrazo compounds fall within its scope. Typical amines of this class are p-phenylene diamine, benzidine, o-tolidine, o-dianisidine, 4,4'-diamino stilbene, 4,4'-diamino diphenylamine, 2,2'-dimethyl-4,4'-diamino diphenylamine and 1,5-diamino naphthalene.

Also diazonium salts derived from heterocyclic amines or diamines fall under the present invention. Typical heterocyclic amines are 2-amino-carbazole, 3,6-diaminocarbazole, 2-nitro-3-aminocarbazole, 2-nitro-3-amino-dibenzofuran, 2-amino-3-nitrobenzothiophene, 1-amino-5-fluorobenzothiazole;




Obviously also mixtures of different diazonium salts may be used.

The inhibitors claimed in this invention comprise the water soluble esters of organic di- and tri-basic carboxylic, sulfonic, and sulfocarboxylic acids, the acid portion being free from olefinic double bonds and acetylenic triple bonds and the alcoholic portion containing at least one olefinic double bond or at least one acetylenic triple bond. The olefinic double bond and the acetylenic triple bonds of the alcoholic portion of the esters which are the inhibitors of the present invention appear to be mainly responsible for the anti-thinning action. We have found that a certain minimum number of these unsaturated bonds are necessary in molecules of given size. Anti-thinning action is not practically effective unless there is at least one olefinic double bond or acetylenic triple bond per 12 carbon atoms of the acid and alcohol portions combined.

The inhibitors of the present invention include water soluble esters of the organic di- and tribasic carboxylic, sulfonic, and sulfocarboxylic acids. It is necessary, however, that neither the acid nor the alcohol portion of the ester contain constituents capable of azoic coupling with the diazonium salt, catalytic decomposition thereof at room temperature, or condensation therewith to form diazoamino or diazoimino compounds in acid medium. It is also necessary that the cations of the water soluble salts of the above esters, where they are used, should likewise be of such nature that they will not couple azoically, catalytically decompose the diazonium salts, or condense to form diazoamino or diazoimino compounds in acid medium. Examples of cations which are objectionable are dimethyl aniline or copper, the latter having a catalytic decomposing effect on diazonium compounds.

Except for the limitations in the preceding paragraphs, any of the unsaturated esters may be used as inhibitors and they may contain one or more olefinic double bond, acetylenic triple bond, or both types of bonds in the same molecule. Mixtures of different esters may also be used.

The polybasic acids are organic with the restriction that they should not contain olefinic double bonds or acetylenic triple bonds and that their acidic groups should be either sulfonic or carboxylic groups or both combined. The acids may be aliphatic and as examples of such aliphatic acids there may be mentioned: oxalic acid, succinic acid, chlorosuccinic acid, malic acid, tartaric acids, tricarballylic acid, citric acid, mesoxalic acid, mucic acid, thiodiacetic acid, sulfoacetic acid, sulfosuccinic acid. The acids may be alicyclic such as the hexahydrophthalic acids. The acids may belong also to the aromatic series, provided they do not couple. As examples of such aromatic polybasic acids there may be mentioned the phthalic acids, trimesic acid, benzene disulfonic acids, m-sulfobenzoic acid, sulfonaphthoic acids. The esters may also derive from polybasic acids of the heterocyclic series such as e. g. quinolinic acid.

The esters may contain more than one alcohol group and it is not necessary that each alcohol group contain the olefinic double bond or acetylenic triple bond, it being sufficient that at least one of the alcohols contains such a bond. The alcohol radicals may contain several un-

saturated bonds. It is unnecessary that the alcoholic oxygen be connected to the unsaturated group by a carbon chain. On the contrary the carbon chain may be interrupted by other elements such as oxygen, nitrogen, sulfur, etc.

The esters may derive from a great number of unsaturated alcohols. The alcohols belonging to the aliphatic series are e. g. vinyl alcohol, allyl alcohol, 2-methyl-2-propanol, 2-butenol, 1,1-dimethyl-2-propenol, 3,3-diethyl-2-propenol, 1,6-heptadienol-1, 3,7-dimethyl-2,6-octadienol-1, propargyl alcohol.

As examples of unsaturated alcohols of the alicyclic series from which the esters of the present invention may derive there may be mentioned e. g. isomeric terpineols, isopulegol. The esters may also derive from aromatic alcohols provided they contain an olefinic double bond or acetylenic triple bond outside the aromatic ring and provided they do not couple. As an example there may be mentioned cinnamyl alcohol. With the same restrictions just mentioned for the aromatic alcohols, the esters may derive also from heterocyclic alcohols.

The alcoholic components as well as the acid components of the esters may be also substituted by various substituents provided, however, that these substituents do not cause azoic coupling with diazo compounds and do not react otherwise with them.

To be useful in this invention the esters must be soluble in acid, aqueous media. The most useful ester derivatives of dibasic acids are therefore the monoesters and the most useful derivatives of tribasic acids are the monoesters and diesters. Typical esters are the following: allyl oxalate, mono allyl succinate, mono allyl tartrate, mono allyl tricarballylate, mono allyl citrate, diallyl mucate, the mono allyl ester of sulfoacetic acid $HO_3SCH_2COOC_3H_5$, sulfosuccinic acid diallyl ester and dimethallyl ester, the mono allyl ester of hexahydro phthalic acid, the mono allyl ester of m-sulfobenzoic acid $HO_3SC_6H_4COOC_3H_5$, the mono allyl ester of quinolinic acid.

It will be noted that a wide choice of esters is available. Many of the esters are with acids having a small number of carbon atoms so that the total ester contains less than 12 carbon atoms. In such cases, as is pointed out above, a single olefinic double bond or acetylenic triple bond is sufficient to confer anti-thinning action on the ester. It will be noted that when some of the higher unsaturated alcohols such as 3,7-dimethyl-2,6-octadienol-1 are used with acids having large numbers of carbon atoms, esters of more than 12 carbon atoms are produced. In such cases as stated above, more than one double or triple bond must be present. For example, if 3,7-dimethyl-2,6-octadienol-1 is esterified with sulfosuccinate acid, a compound is obtained having 14 carbon atoms and four double bonds and when the two molecules of the acid are esterified with trimesic which is one of the acids listed, an ester is obtained having 29 carbon atoms and four double bonds.

The esters still containing an acidic group may be employed as such or preferentially in the form of water soluble salts. Since the active principle is the anion of the unsaturated ester acid it is in many cases more convenient to use their water soluble salts because they are easier to prepare and handle. There are, of course, a great number of bases that will form such water soluble salts with the acid esters of this invention and they all may be used with only two principal exceptions. The first one is that they should not catalytically decompose diazo compounds as for example copper salts are known to do. Secondly, if the ester acid is combined with an aromatic base the latter must be so chosen that it does not couple. In the third plan the base should not form diazoamino or diazoimino compounds in acid medium. The sodium and potassium salts of the ester acids claimed in this invention are the cheapest and the most convenient ones to prepare, but in some cases salts with other metals such as for example zinc or calcium, ammonium salts and salts with various organic bases such as amines, amidines, guanidines, etc., may be used.

The inhibitors of the present invention may be added in two stages, either before or after the diazotization. In the first place the aromatic bases known as ice color diazo components may be blended with the inhibitor and such blends may be subsequently diazotized in the customary manner and incorporated into a printing paste. The obvious equivalent of this procedure is to dissolve the inhibitor and the base separately before the diazotization. If the inhibitors are used in this manner they obviously should not contain diazotizable amino groups. In the second place diazonium salts, either stable per se or stabilized in a customary way, may be blended with the inhibitor. The obvious equivalent is to add the inhibitor to a separately prepared diazo solution before the printing paste is made up. It does not make any difference what procedure is used in every case the thinning of the gum is greatly delayed.

If the diazonium salt is first mixed with the printing gum and the inhibitor is added afterwards, then in a great many cases of very active diazo compounds a certain amount of thinning has already taken place before the inhibitor is added. This procedure, therefore, should be used only where the thinning action is slow, but it is included in the broad scope of the invention.

The invention will be further illustrated with the specific examples which describe typical embodiments of the present invention. The parts are by weight.

*Example 1*

A paste is made up as follows: 5.48 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 3-nitro-4-amino-anisole and partially dehydrated aluminum sulfate corresponding to 15.35% of real base, is dissolved in 21 parts of water, and there is added to the mixture 0.274 part of monoallyl succinate of the following formula:

$$CH_2{=}CH{-}CH_2{-}OOC{-}CH_2{-}CH_2{-}COOH$$

This solution is then intimately mixed with 75 parts of a 2½% aqueous carob bean gum. This resulting printing paste is suitable for the preparation of fast color patterns printed in the customary manner on cloth impregnated with the usual ice color coupling components such as arylides of 2,3-hydroxy-naphthoic acid, etc.

The relative viscosity of such printing gum can be determined in a number of different ways. A very simple and convenient method of measurement, the one which was used with this example, consists in allowing copper plated steel balls to fall through a measured distance of the printing gum; for example, 130 millimeters, and timing the fall with a stop watch. In this example, the

so-called units of relative viscosity are the times in seconds for copper plated steel balls weighing approximately 0.107 gram each to fall 130 mm. through the gum at approximately 25° C.

The beneficial effect of the ester on the preservation of the viscosity of this bum can be seen from the following table:

| Printing gum used | Relative viscosity 2 minutes after mixing | Relative viscosity 2 hours after mixing |
|---|---|---|
| Paste made as in Example 1 | 81 | 29.8 |
| Same but without ester | 67 | 0.5 |

The monoallyl succinate used in this example is prepared by refluxing equimolecular quantities of succinic anhydride and allyl alcohol for three hours in the presence of pyridine. The product is purified by distillation in a vacuum. It boils at 119° C. at 2 mm.

*Example 2*

A solution is made of 1.25 parts of the zinc chloride double salt of the diazonium chloride derived from 3-nitro-4-amino-onisole, 2.74 parts of monoallyl succinate and 21 parts of water. This solution is then intimately mixed with 75 parts of a gum tragacanth paste containing 3 parts of dry gum per 100 parts of finished paste. The resulting printing paste is suitable for the production of fast color prints on textiles impregnated with ice color coupling components in the usual manner. The beneficial effects of the monoallyl succinate in preserving the viscosity of the printing gum are shown in the following table:

| Printing gum used | Relative viscosity after 2 minutes | Relative viscosity after 2 hours |
|---|---|---|
| Printing paste as described above | 130 | 124 |
| Same but without ester | 121 | 92 |

The relative viscosity readings obtained in these examples were obtained by the use of a Brookfield Viscosimeter.

Instead of using gum tragacanth, other gums of vegetable origin may be used. For example, the solution of diazonium zinc chloride double salt, inhibitor and water as described above in this example, is mixed with 75 parts of methyl cellulose gum prepared as follows:

30 parts of methyl cellulose of the brand known as "Methocel 4000" is added slowly to 1000 parts of boiling water with stirring. The mixture is allowed to cool to room temperature with constant stirring and a clear viscous gum is thus obtained. The resulting mixture, which is useful for the production of fast color prints on cloth in a manner indicated previously, preserves its relative viscosity much better than a similar paste which does not contain the ester, as is shown in the following table:

| Printing gum used | Relative viscosity measurement after 2 minutes | Relative viscosity measurement after 21 hours |
|---|---|---|
| Printing paste as described above | 38.1 | 29.1 |
| Same but containing no ester | 40.5 | 7.2 |

The relative viscosity figures for the paste made of the methyl cellulose are the number of seconds for copper plated steel balls weighing approximately 0.358 gram to fall through 130 millimeters of paste.

*Example 3*

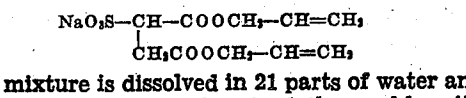
Printing pastes are made by dissolving 0.005 equivalent part of real diazotized or tetrazotized ice color base in the form of its zinc chloride double salt, together with 0.274 part of monoallyl succinate, in 21 parts of water, and then intimately mixing the resulting solution with 75 parts of 2% carob bean gum. The resulting printing pastes are used for the production of fast color prints on cotton cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. These pastes retain their relative viscosity longer, and hence are of far greater practical utility to the printer, than similar printing pastes which do not contain the monoallyl succinate. This advantage is shown in the following table:

| Base used for $ZnCl_2$ double salt | Inhibitor | Relative viscosity measurement after 2 min. | Relative viscosity measurement after 2 hr. | Color of print on anilide of 2-hydroxy-3-naphthoic acid |
|---|---|---|---|---|
| 2,5-dichloraniline | Yes | 55.6 | 50.6 | Yellowish scarlet. |
| 2,5-dichloraniline | No | 51.4 | 16.3 | Do. |
| 4-nitro-2-amino anisole | Yes | 53.4 | 47.7 | Reddish scarlet. |
| 4-nitro-2-amino anisole | No | 53.2 | 23.9 | Do. |
| o-Dianisidine | Yes | 52.2 | 43.6 | Navy blue. |
| o-Dianisidine | No | 52.8 | 22.1 | Do. |

These relative viscosity measurements are the times in seconds for spherical glass beads weighing 0.097 gram each to fall 130 mm. through the paste.

*Example 4*

A printing paste is made by mixing 1.95 parts of the zinc chloride double salt of the diazonium chloride obtained from 3-nitro-4-amino-anisole, corresponding to 47.3% real base, and 0.519 part of diallyl sodium sulfosuccinate of the following formula:



This mixture is dissolved in 21 parts of water and the resulting solution is mixed thoroughly with 75 parts of 2% carob bean gum. This printing paste is used for printing fast color patterns upon cloth impregnated with ice color coupling components in the usual manner.

A printing paste is made in exactly the same manner but with 1.65 parts of the zinc chloride double salt obtained from the diazonium chloride of 2,5-dichloroaniline substituted for the analogous salt obtained from 3-nitro-4-amino-anisole. This printing paste is used for printing in a similar manner.

In an entirely similar manner, a printing paste is made from 1.54 parts of the zinc chloride double salt derived from the diazonium chloride of 4-nitro-2-amino-anisole, the other ingredients being the same as those indicated above.

The three printing pastes prepared as described above all possess the advantageous property of retaining their relative viscosities, and hence their utility for printing, much longer than similar pastes which are prepared in a like manner but without the diallyl sodium sulfosuccinate. This is shown in the following table:

| Base used for diazo | Inhibitor used | Relative viscosity reading after 2 min. | Relative viscosity reading after 4 hrs. | Color of print on anilide of 2-hydroxy-3-naphthoic acid |
|---|---|---|---|---|
| 3-nitro-4-amino anisole | Diallyl Na sulfo-succinate | 65.2 | 26.2 | Bordeaux. |
| 3-nitro-4-amino anisole | O | 62.6 | 0.6 | Do. |
| 2, 5-dichlor aniline | Diallyl Na sulfo-succinate | 46.0 | 41.7 | Yellowish Scarlet. |
| 2, 5-dichlor aniline | O | 41.7 | 18.2 | Do. |
| 4-nitro-2-amino anisole | Diallyl Na sulfo-succinate | 44.8 | 35.7 | Reddish Scarlet. |
| 4-nitro-2-amino anisole | O | 46.8 | 21.6 | Do. |

The relative viscosity readings in the above table are the times in seconds for spherical glass beads weighing 0.097 gram each to fall 130 millimeters.

The diallyl sodium sulfosuccinate of this example was prepared from diallyl maleate and bisulfite by the method described in U. S. Patent No. 2,028,091.

This application is in part a continuation of our co-pending application, Serial No. 437,200, filed April 1, 1942.

We claim:

1. Diazo compounds suitable for printing, containing a water soluble diazonium salt derived from an ice color diazo component and a water soluble ester, the acid portion being included in the group consisting of organic di- and tri-basic carboxylic acids, organic di- and tri-basic sulfonic acids, organic di- and tri-basic sulfocarboxylic acids, and their water soluble salts, the acids being free from olefinic double bonds and acetylenic triple bonds and the alcoholic portion of the ester being included in the group consisting of alcohols containing at least one olefinic double bond and alcohols containing at least one acetylenic triple bond, the total number of double and triple bonds being at least one for 12 carbon atoms of the acid and alcoholic portions of the esters combined, the esters being free from constituents capable of azoic coupling with the diazonium salts, catalytic decomposition thereof at room temperature, or condensation therewith to form diazoamino or diazoimino compounds in acid medium, and the amount of ester being sufficient to substantially inhibit thinning of a carbohydrate thickener.

2. Printing pastes containing a carbohydrate thickener and at least one water soluble diazonium salt derived from an ice color diazo component and a water soluble ester, the acid portion being included in the group consisting of organic di- and tri-basic carboxylic acids, organic di- and tri-basic sulfonic acids, organic di- and tri-basic sulfocarboxylic acids, and their water soluble salts, the acids being free from olefinic double bonds and acetylenic triple bonds and the alcoholic portion of the ester being included in the group consisting of alcohols containing at least one olefinic double bond and alcohols containing at least one acetylenic triple bond, the total number of double and triple bonds being at least one for 12 carbon atoms of the acid and alcoholic portions of the esters combined, the esters being free from constituents capable of azoic coupling with the diazonium salts, catalytic decomposition thereof at room temperature, or condensation therewith to form diazoamino or diazoimino compounds in acid medium, and the amount of ester being sufficient to substantially inhibit thinning of the carbohydrate thickener.

3. A composition according to claim 1 in which the diazonium salt is the diazonium chloride-zinc chloride double salt.

4. A composition according to claim 2 in which the diazonium salt is the diazonium chloride-zinc chloride double salt.

5. A composition according to claim 2 in which the ester is a diallylsulfosuccinate.

6. A composition according to claim 2 in which the ester is a bis-(beta-methyl-allyl) sulfosuccinate.

7. A composition suitable for the preparation of printing pastes containing carbohydrate gum thickeners comprising an ice color forming component included in the group consisting of compositions containing water soluble diazonium salts and intermediates therefor consisting of amines diazotizable to produce compositions containing water soluble diazonium salts, the color forming component having admixed therewith a water soluble ester, the acid portion being selected from the group consisting of organic di- and tri-basic carboxylic acids, organic di- and tri-basic sulfonic acids, organic di- and tri-basic sulfocarboxylic acids, and their water soluble salts, the acids being free from olefinic double bonds and acetylenic triple bonds, and the alcoholic portion of the ester being selected from the group consisting of alcohols containing at least one olefinic double bond and alcohols containing at least one acetylenic triple bond, the total number of double and triple bonds being at least one for each 12 carbon atoms of the acid and alcoholic portions of the esters combined, the esters being free from constituents capable of azoic coupling with the diazonium salts, of catalytically decomposing them at room temperature, or condensing with them to form diazo amino or diazo imino compounds in acid medium, and the amount of ester being sufficient to substantially inhibit thinning of a carbohydrate thickener.

8. A composition according to claim 1 in which the ester is a diallyl sulfosuccinate.

9. A composition according to claim 1 in which the ester is a bis-(betamethyl-allyl)-sulfosuccinate.

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