

## UNITED STATES PATENT OFFICE

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## STABILIZATION OF COLORING COMPOSITIONS CONTAINING DIAZONIUM SALTS

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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.

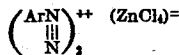
According to the present invention the diazonium salt is associated with an organic nitrogenous base soluble in aqueous mineral acids and containing at least one olefinic double bond or one acetylenic triple bond for each 12 carbon atoms.

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



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 explosiveness, others are rather stable and do not present an explosive hazard. It is also known that if the anion of the acid X<sup>-</sup> 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 salts is sometimes referred to as "stabilized" diazonium salts. They comprise such compounds as certain aromatic sulfonates, without olefinic

doubled 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:



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 diazo amino and diazo imino 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 diazo amino or diazo imino 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 beta-naphthol 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 deriving 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 compounds. On the other hand the diazonium salts deriving from the 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 celluloses. 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 these thickeners are carbohydrates or carbohydrate derivatives. In the claims the expression "carbohydrate thickener" is used in a broad sense to cover pure carbohydrates and derivatives.

We have found that organic nitrogenous bases that are soluble in aqueous mineral acids and that contain at least one olefinic double bond or one acetylenic triple bond for each 12 carbon atoms or their water soluble salts delay the thinning to such an extent that it becomes harmless from the practical point of view.

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 an unsaturated nitrogenous base 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 a 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.

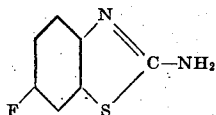
The present invention includes all the diazonium salts derived from ice color diazo components, that is to say, from all diazotizable aromatic amines free from solubilizing groups useful in making ice colors or azoic pigments. Typical are the following:

10 Aniline and its homologues, as e. g. the toluidines, 2,4-dimethylaniline; halogen derivatives of aniline and of its homologues, as e. g. the mono-fluoroanilines, the monochloranilines, 2,5-difluoroaniline, 2-fluoro-5-chloroaniline, 2,5-dichloroaniline, m-aminobenzotrifluoride, p-amino-benzotrifluoride, 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-methylaniline, 2,5-dimethoxy-aniline, 2-methoxy-1-naphthylamine, 2-amino-diphenyl-ether, 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-ethoxyaniline, 4-chloro-2-amino-diphenylether, 4-amino-2-chloro-diphenylether, 4-amino-4'-chloro-diphenyl ether, 4,4'-dichloro-2-amino-diphenylether, 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-methoxyaniline, 2-methoxy-4-nitro-5-methylaniline; 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-phenoxyacetylamino-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-alkoxytoluenes and of 2,5-diamino-4-alkoxy-chlorobenzenes and of 2,5-diamino-4-alkoxy-benzene sulfodialkylamides; analogous monoacyl derivatives of 1,3-diamino-4,5-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'-chloroazobenzene, 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 deriving 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 2,6-dichloro-1,4-phenylene diamine. Diazonium salts deriving 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 deriving 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-aminodibenzofuran, 2-amino-3-nitrobenzothiophene, 1-amino-5-fluorobenzothiazole.



Obviously also mixtures of different diazonium salts may be used.

The inhibitors claimed in the present invention comprise all organic nitrogenous bases that are soluble in aqueous mineral acids and that contain at least one olefinic double bond or at least one acetylenic triple bond. We have found that the olefinic double bond or acetylenic triple bond appears to be mainly responsible for the anti-thinning action of the nitrogenous bases of the present invention. However, we have found that there is a lower limit for the number of such unsaturated bonds in a molecule of given size. Practically useful inhibiting action is obtained only if there is at least one olefinic double bond or acetylenic triple bond for each 12 carbon atoms of the nitrogenous base. In addition to the above limitation on the nitrogenous base, it is necessary that the base be soluble in mineral acids since the printing pastes containing the diazonium salts are always acid. The bases may be used as such if there is sufficient acid in the printing paste to both neutralize and dissolve them, or they may be used in the form of any of their water soluble salts. In fact in the printing paste they undoubtedly exist in the form of their water soluble

salts regardless of the form in which they are introduced. It is also necessary that the bases and their salts be free from constituents capable of azoic coupling with the diazonium salt, condensation therewith to form diazoamino or diazoimino compounds in acid medium, or catalytic decomposition thereof at room temperatures. The second limitation is not a serious one as it is difficult to form a diazoamino or diazoimino compound under the acid conditions which obtain in the compositions of the present invention. Examples of compounds which catalytically decompose the diazonium salts are iodides of the inhibiting bases. The inhibitors may contain one or more basic nitrogenous groups and, of course, they may contain one or more olefinic double bonds or acetylenic triple bonds. The same molecule may also contain both kinds of bonds. The portion of the molecule containing the unsaturated bonds may be connected to the basic nitrogenous groups through a carbon chain or a carbon chain interrupted by other elements such as oxygen, nitrogen, sulfur, and the like. The invention is not limited to the use of any single inhibitor and mixtures may be employed where desired.

The organic nitrogenous bases may be divided into two main groups. In the first group the basic portion of the molecule contains only one nitrogen atom connected with the same carbon atom and this group comprises the primary, secondary and tertiary amines and the quaternary bases. It also comprises compounds which contain two or more such groups which, however, are not connected with the same carbon atom. In the second group the basic part of the molecule contains two or three nitrogen atoms connected with the same carbon atom and this group comprises amidines and the closely related isoureas, isothiouras, guanidines, ureas, etc.

As examples of aliphatic bases of the first group there may be mentioned: allylamine, N-methyl-N-allylamine, diallylamine, N,N-dimethyl-N-allylamine, triallylamine, N,N,N-trimethyl-N-allyl ammonium hydroxide, tetra-allyl ammonium hydroxide, N,N,N-triethyl allyl ammonium hydroxide, N-propyl-N-allylamine, N-methyl-N-propyl-N-allylamine, N-isobutyl-N-allylamine, N-beta-methyl-allyl trimethyl ammonium hydroxide, N-gamma-methyl-allylamine, 4-amino-pentene-1, 5-amino-hexene-1, 4-allyl-5-amino-pentene-1, 2,6-dimethyl-8-amino octadiene-2,6, (beta-amino ethyl)-allyl ether and thio ether, 2-propynylamine (propargylamine), N,N,N',N'-tetra-allyl ethylene diamine.

As examples of aliphatic bases belonging to the second group there may be mentioned N-allylurea, N-ethyl-N'-allylurea, N,N'-diallylurea, O-allyl isourea, S-allyl isothiouras, S-beta-methyl-allyl isothiouras, allyl guanidine, omega-allyl-bis-guanidine.

It is not necessary that the bases of the present invention belong to the aliphatic series, and bases having ring systems are also included, provided they contain at least one double bond of olefinic character or at least one triple bond. It should be noted that double bonds occurring in aromatic rings are not of olefinic nature. Thus N-phenyl-N,N,N-trimethyl ammonium hydroxide is not an inhibitor covered by the present invention because the benzene ring does not contain olefinic double bonds. However, unsaturated alicyclic bases are active inhibitors such as, for example, 4-amino cyclohexene-1, 3-N,N-dimethylamino cyclohexene-1 and the corresponding quaternary ammo-

nium base containing one methyl more on the nitrogen, 5-amino cyclo-octene-1, 6-amino-para-menthene-1, 2-amino-para-menthene-8.

Also aromatic amines are useful provided they contain an unsaturated olefinic or acetylenic bond outside the aromatic ring and provided they are not capable of azoic coupling; as examples of such compounds there may be mentioned N-allyl - N,N - dimethyl - N - phenyl ammonium hydroxide, N,N-diallyl-para-chloroaniline, N,N,N-triallyl - N - para-tolyl ammonium hydroxide, (which compound, it will be noted, contains 16 carbon atoms and 3 olefinic double bonds), N-propargyl - N,N-dimethyl-N-phenyl ammonium hydroxide.

Also heterocyclic bases are useful provided they contain double bonds of olefinic character either in the ring or outside the ring, or provided they contain outside the ring acetylenic triple bonds and also provided they do not couple. As examples of such compounds there may be mentioned N,N-diallyl furfurylamine, N,N-diallyl-6-amino-1,4-benzodioxane, tropidine, N-allyl pyridinium hydroxide.

The inhibitors of the present invention may be added either before or after the diazotization. However, not all of the inhibitors claimed in this invention can be added before the diazotization because a great many of them would react with nitrous acid. Thus, all primary and secondary amines cannot be added before the diazotization. If the inhibitor is to be added before the diazotization we therefore prefer to use aliphatic tertiary or quaternary compounds. In this case 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 ice color diazo component separately before the diazotization is carried out.

When the inhibitor is added after diazotization also a primary or secondary amine may be used. Since printing pastes containing diazonium salts are acid, no formation of diazo-amino or diazo-imino compounds or of analogous condensation products with amidines or guanidines takes place. Diazonium salts either stable per se or stabilized in a customary manner 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 printing 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.

Since the active anti-thinning principle is part of the basic portion of the molecule, it does not make any difference whether the base is used as such or whether a water soluble salt is used. It is however, very difficult to isolate quaternary bases and in most cases they can not be isolated at all, and therefore in practically all cases dealing with quaternary bases, they are preferably employed in the form of their salts. Also in the cases of a great many other bases, particularly those that are liquid, the use of salts is preferable

whenever a dry blend with either the ice color diazo component or with the diazonium salt is to be made. Obviously the salts must be water soluble, but it is not necessary that the corresponding base is water soluble since the free base would be liberated only after the diazonium salt has been printed on the naphthol prepared goods and after the inhibitor had already accomplished its task of keeping the printing paste stable.

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

2.56 parts of the zinc chloride double salt of the tetrazonium chloride derived from o-dianisidine, diluted with partially dehydrated magnesium sulfate so as to correspond to 29.8% of real base, are mixed with 0.2 part of N-allyl-N,N,N-triethyl ammonium chloride and the mixture is dissolved in 22.3 parts of water. This solution is intimately mixed with 75 parts of 2.5% carob bean gum. The printing paste thus made is used for printing blue patterns upon cellulosic material which has been impregnated with arylides of 2-hydroxy-3-naphthoic acid. It has the advantage over a paste not containing the allyl triethyl ammonium chloride that the former retains its viscosity better than the latter, as is shown by the following figures:

Printing paste used	Relative viscosity measurement after half an hour	Relative viscosity measurement after 4.7 hours
Printing paste as described above.....	33.0	17.0
Same but without inhibitor.....	26.5	3.5

In this experiment the relative viscosities are measured by noting the time for lead shot weighing .071 gram each to fall 130 millimeters through the paste.

#### Example 2

25 parts of a solution of diazotized 5-nitro-2-amino anisole, equivalent to 0.84 part of real base, are mixed with a solution of 0.256 parts of N-allyl-N,N,N-triethyl ammonium chloride in 11.6 parts of water and the resulting solution is thoroughly mixed with 75 parts of 2.5% carob bean gum. This paste is used for the production of fast red prints on cotton cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. The advantage of this paste over one similarly prepared but without the N-allyl-N,N,N-triethyl ammonium chloride is shown in the following table:

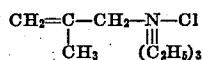
Printing paste used	Relative viscosity measurement after three minutes	Relative viscosity measurement after three hours
Printing paste as described above.....	19.6	14.2
Same, but without inhibitor.....	20.0	10.8

These relative viscosity measurements are the times in seconds for copper plated steel shot weighing 0.107 gram each to fall 130 millimeters.

Instead of the N-allyl-N,N,N-triethyl ammonium chloride, other water soluble salts such as the sulfate, phosphate, nitrate, ethane sulfonate, benzene sulfonate, succinate, etc., may be used with equal success.

### Example 3

1.62 parts of the zinc chloride double salt of the diazonium chloride obtained from 2,5-dichloroaniline, corresponding to approximately 50% real base, and 0.331 part of N-beta-methyl-allyl-N,N,N-triethyl ammonium chloride of the following formula:



are dissolved in 21 parts of water, and the resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. The resulting printing paste is used for the preparation of fast

the production of fast prints on fibers impregnated with the usual ice color coupling components in the usual manner. In each case the relative viscosity of the printing paste so prepared decreased less rapidly than the relative viscosity of similar printing pastes prepared without the addition of the quaternary salt used as inhibitor.

In the following table the relative viscosities of such printing gums, measured when freshly made and after a certain length of time, are compared with the relative viscosities of similar gums not containing the inhibitor taken at the same time:

Nature of printing powder	Parts of water to dissolve	Kind of thickening gum used	Strength of thickening gum	Relative viscosity reading after 2 minutes	Time after mixing of second relative viscosity measurement	Second relative viscosity measurement	Method of relative viscosity measurement
			Percent		Hours		
Contains inhibitor	21	Carob bean	2.5	56.5	1	39.4	A
Without inhibitor	21	do	2.5	57.8	1	2.1	A
With inhibitor	21	Methyl cellulose (Methocel 4000)	3.0	39.8	21	24.4	A
Without inhibitor	21	do	3.0	40.5	21	7.2	A
With inhibitor	23	Sweet potato starch	5.25	34.5	3	34.4	B
Without inhibitor	23	do	5.25	35.0	3	28.0	B
With inhibitor	21	Gum tragacanth	3.5	121.0	4	107.0	C
Without inhibitor	21	do	3.5	121.0	4	57.0	C

NOTE.—Method "A" consists of the measurement of the time in seconds for glass beads weighing 0.097 gram to fall 130 millimeters through the gum. Method "B" consists in timing in seconds the flow of 10 cc. of the paste from a 10 cc. pipette. Method "C" consists of readings taken on a Brookfield electric viscosimeter—speed 60, spindle No. 3.

scarlet prints upon cotton cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid and for the preparation of fast orange prints upon cotton cloth impregnated with the ortho phenetidine of 2-hydroxy-3-naphthoic acid in the well-known manner. The printing paste so prepared retains its relative viscosity, and hence its utility for printing much better than a similar paste which does not contain the N-beta-methyl-allyl-N,N,N-triethyl ammonium chloride, as is shown by the following figures:

Printing paste used	Relative viscosity measurement after two minutes	Relative viscosity measurement after four hours
Printing paste as described above	41.4	33.2
Same but without inhibitor	41.3	17.9

### Example 4

Printing pastes are made by dissolving in water the number of parts of the zinc chloride double salt of the diazonium chloride obtained from 3-nitro-4-amino anisole equivalent to 0.84 part of real base and 0.331 part of N-beta-methyl-allyl-N,N,N-triethyl ammonium chloride, and the resulting solutions are mixed with various aqueous printing gums. These gums can be used for

### Example 5

3.86 parts of a mixture of the zinc chloride double salt of the diazonium chloride obtained from 3-nitro-4-amino anisole and partially dehydrated magnesium sulfate, corresponding to 21.6% of real base, is mixed with 0.288 part of N-vinyl-N,N,N-trimethyl ammonium bromide (neurine bromide). The mixture is then dissolved in 21 parts of water and the resulting solution is thoroughly mixed with 75 parts of 2.5% carob bean gum. The resulting paste is used for the production of fast color prints upon fibers impregnated with ice color coupling components in the usual manner.

In a similar manner a printing paste is made from 1.62 parts of the zinc chloride double salt of the diazonium chloride of 2,5-dichloroaniline, 0.288 part of N-vinyl-N,N,N-trimethyl ammonium bromide, 21 parts of water, and 75 parts of 2.5% carob bean gum. This paste is used for the production of fast color prints in impregnated cloth in the manner described above.

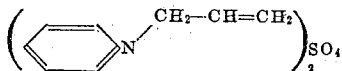
The advantages which these printing pastes containing the N-vinyl-N,N,N-trimethyl ammonium bromide have over similar pastes without this salt lie in the fact that the former printing pastes do not decrease in relative viscosity as rapidly as the latter. This is shown in the following table:

Base used for diazo	Nature of printing paste	Time after mixing for first relative viscosity reading	First relative viscosity reading	Time after mixing of second relative viscosity reading	Second relative viscosity reading
		Minutes		Hours	
3-nitro-4-amino anisole	With inhibitor	2	58.9	2	12.8
Do	Without inhibitor	2	55.2	2	1.2
2,5-dichloroaniline	With inhibitor	8	61.8	3	41.0
Do	Without inhibitor	8	52.7	3	21.3

The relative viscosity readings are the times in seconds for spherical glass beads weighing 0.0975 gram each to fall 130 mm. through the gum.

### Example 6

2.54 parts of the mixture of the zinc chloride double salt of the tetrazonium chloride derived from *o*-dianisidine and partially dehydrated magnesium sulfate, having a strength equivalent to 29.8% real base, are mixed with 0.3 part of *N*-allyl pyridinium sulfate of the following formula:



and the mixture is dissolved in 22.1 parts of water. The resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. In an entirely analogous manner, a printing paste is made from the same ingredients except that *N*-allyl pyridinium chloride (0.24 part) is used instead of the sulfate. These printing pastes are used for the preparation of fast blue prints on cellulosic fiber impregnated with the anilide of 2-hydroxy-3-naphthoic acid. These pastes decrease more slowly in relative viscosity, and hence retain their utility for printing for a longer time than similar pastes made without the water soluble salt of the organic nitrogenous base, as is shown in the following table:

Inhibitor used	Relative viscosity reading $\frac{1}{2}$ hour after mixing	Relative viscosity reading $4\frac{1}{2}$ hours after mixing
<i>N</i> -allyl pyridinium sulfate.....	29.9	17.1
<i>N</i> -allyl pyridinium chloride.....	27.5	13.3
None.....	26.5	3.5

These viscosity measurements are the times in seconds for lead shot weighing 0.071 gram each to fall 130 millimeters.

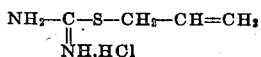
### Example 7

A mixture is made of 1.62 parts of the zinc chloride double salt of the diazonium chloride derived

Nature of printing powder	Water to dissolve printing powder	Thickening gum used	Strength of gum in percent	Time of first relative viscosity reading after mixing	First relative viscosity reading	Time of second relative viscosity reading after mixing	Second relative viscosity reading	Method of relative viscosity determination
With inhibitor.....	21	Carob bean.....	2.5	Minutes	2	Hours	1	A
Without inhibitor.....	21	do.....	2.5					
With inhibitor.....	21	Methyl cellulose (Methocel 4000).....	3	2	57.8	1	2.1	A
Without inhibitor.....	21	do.....	3	2	40.7	4	30.8	A
With inhibitor.....	23	Sweet potato starch.....	5.26	2	46.5	4	20.4	A
Without inhibitor.....	23	do.....	5.26	2	34.2	3	34.1	B
With inhibitor.....	21	Gum tragacanth.....	3.5	3	117	4	98	C1
Without inhibitor.....	21	do.....	3.5	3	121	4	57	C1
With inhibitor.....	21	R. P. G. gum (mixed starches).....	8	4	750	4	730	C2
Without inhibitor.....	21	do.....	8	4	600	4	335	C2

NOTE.—Relative viscosity measurements are taken as follows: A—Time in seconds for glass beads weighing .0975 gram to fall 130 mm. B—Time in seconds for 10 cc. of paste to flow from a 10 cc. pipette. C1—Relative reading taken on Brookfield electric viscosimeter. C2—Reading in centipoises taken on Brookfield viscosimeter.

from 2,5-dichloroaniline and 0.264 part of allyl isothiourea hydrochloride of the following formula:



This mixture is dissolved in 21 parts of water, and the resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. This printing paste is eminently suited for the production of fast color prints upon cloth impregnated with the usual ice color coupling components;

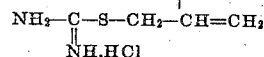
for example, for the production of fast bright scarlet prints on cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid; for the production of bright reddish orange prints on cloth impregnated with the ortho phenetidide of 2-hydroxy-3-naphthoic acid; or for the production of bright yellow prints on cloth impregnated with bis-acetoacetic acid *o*-tolidide. The beneficial effect of the allyl isothiourea hydrochloride on maintaining the relative viscosity of the printing paste is shown in the following table:

Printing paste used	Relative viscosity reading after 2 minutes	Relative viscosity reading after 4 hours
Printing paste as described above.....	41.7	33.8
Same but without allyl isothiourea.....	41.3	17.9

These relative viscosity measurements are the times in seconds for special glass beads weighing 0.0975 gram each to fall 130 mm.

### Example 8

Solutions are made by dissolving in 21 parts of water an amount of the zinc chloride double salt of the diazonium chloride derived from 3-nitro-4-amino anisole equivalent to 0.84 part of real base and 0.264 part of allyl isothiourea hydrochloride of the following formula:



Each solution is mixed with 75 parts of an aqueous gum thickener of vegetable origin. These printing pastes are suitable for the preparation of fast color prints on fiber impregnated with ice color coupling components in the usual manner. They are distinguished for their ability to retain their relative viscosity, and hence their utility for printing a longer time than similar pastes prepared without the presence of the allyl isothiourea hydrochloride. This is shown in the following table:

### Example 9

An intimate mixture is made of 10 parts of 3-nitro-4-amino anisole, 2.5 parts of allyl isothiourea hydrochloride, and 7.5 parts of common salt. This mixture is useful for the preparation of fast prints on fibers impregnated with ice color coupling components, as is shown in the following example:

1.68 parts of the mixture described above is stirred in a mixture of 5 parts of 5N hydrochloric acid, 10 parts of ice water, and to the mixture

is gradually added 5 parts of N/1 sodium nitrite solution. After diazotization is complete, the acidity to Congo red paper is destroyed by the addition of small amount of sodium acetate solution. The resulting diazo solution is intimately mixed with 75 parts of 2% aqueous carob bean gum. The resulting viscous paste is printed upon cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid in the customary manner. Bright Bordeaux prints are obtained. After four hours, such a printing gum is still sufficiently viscous for proper printing, whereas a similar paste made from a base not mixed with the inhibitor has become watery and unsuitable for

#### Example 11

In a manner similar to that described in Example 8 printing pastes are made from the zinc chloride double salt of the diazonium chloride of 3-nitro-4-amino anisole and various gum thickeners, but with 0.288 part of beta-methyl allyl isothioureia hydrochloride substituted for the allyl isothioureia used in Example 8. The resulting printing gums are used for preparation of fast color prints upon the fiber prepared with the usual ice color coupling components, and as in the example shown above, these printing pastes maintain their relative viscosity better than similar printing pastes which do not contain the inhibitor. This is shown by the following table:

Nature of printing powder	Parts of water to dissolve printing powder	Thickening gum used	Strength of gum in per cent	Time after mixing of first relative viscosity reading	First relative viscosity reading	Time after mixing of second relative viscosity reading	Second relative viscosity reading	Method of relative viscosity measurement
				Minutes		Hours		
With inhibitor	21	Carob bean	2.5	2	52.3	1	48.0	A
Without inhibitor	21	do	2.5	2	57.8	1	2.1	A
With inhibitor	21	Methyl cellulose (Methocel 4000)	3	2	42.2	4	33.1	A
Without inhibitor	21	do	3	2	40.5	4	20.4	A
With inhibitor	23	Sweet potato starch	5.26	2	33.4	3	34.3	B
Without inhibitor	23	do	5.26	2	35.0	3	28.0	B
With inhibitor	21	Gum tragacanth	3.5	3	120	4	102	C1
Without inhibitor	21	do	3.5	3	121	4	57	C1
With inhibitor	21	R. P. G. gum mixed starches	8	4	745	4	735	C2
Without inhibitor	21	do	8	4	600	4	335	C2

NOTE.—Explanation of viscosity measurements: A—Time in seconds for glass beads weighing 0.097 gram to fall 130 mm. B—Time for 10 cc. of paste to flow from a 10 cc. pipette. C1—Relative readings taken on Brookfield viscosimeter. C2—Reading in centipoises taken on Brookfield viscosimeter.

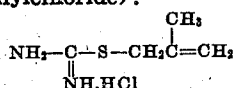
printing. This change in relative viscosity of the gum is shown by the following figures:

Printing gum used	Relative viscosity after 2 min.	Relative viscosity after 4 hours
Printing paste as described above	43.2	21.1
Same but without inhibitor	32.8	2.9

These relative viscosity measurements are the times in seconds taken for glass beads weighing 0.097 gram to fall 130 millimeters.

#### Example 10

A printing gum is made as described in Example 7 except for the fact that 0.288 parts of beta-methyl allyl isothioureia hydrochloride of the following formula (obtainable from thioureia and beta-methylallylchloride):



is used in place of 0.264 part of allyl isothioureia hydrochloride. This printing paste is used for the preparation of fast prints upon fibers impregnated with ice color coupling components in the same manner as that described in Example 7 and the paste has the same remarkable quality of preserving its relative viscosity for a longer period than similar paste not containing the inhibitor. This is shown in the following table:

Printing paste used	Relative viscosity after 2 min.	Relative viscosity after 4 hours
Paste as described above	42.0	34.4
Same but without inhibitor	41.3	17.9

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

#### Example 12

An intimate mixture is made of 10 parts of 5 nitro-2-amino anisole, 8.5 parts of finely powdered Epsom salt, and 2.5 parts of beta-methyl allyl isothioureia hydrochloride. This mixture is diazotized and the resulting diazo solution is mixed with a 2.5% aqueous carob bean gum in the same manner as that described in Example 9 above. The printing paste thus prepared is useful for the preparation of fast color prints on the fiber which has been impregnated with ice color coupling components; for example, when this paste is printed upon cotton cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid, bright bluish red prints of very good fastness properties are produced. The ability of such a paste to maintain its relative viscosity, and hence its utility for printing is shown in the following table:

Printing paste used	Relative viscosity reading after 2 min.	Relative viscosity reading after 4 hours
Paste containing inhibitor	39.2	29.1
Same but without inhibitor	38.2	9.1

These relative viscosity readings indicate the time in seconds for glass beads weighing 0.097 gram to fall 130 millimeters.

#### Example 13

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% real base, is dissolved in 21 parts of water along with 0.162 part of allylamine hydrochloride. The resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum to make a printing paste which is suitable for the production of fast Bor-

deaux prints on cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. This printing paste maintains its relative viscosity, and hence its utility for printing, much better than a similar printing paste which does not contain the allylamine hydrochloride. This advantage is shown in the following table:

Printing paste used	Relative viscosity reading 2 min. after mixing	Relative viscosity reading 2 hours after mixing
Containing allylamine hydrochloride.....	38.5	14.6
Without allylamine hydrochloride.....	40.1	1.4

The relative viscosity readings are the times in seconds for copper plated steel shot weighing 0.107 gram each to fall 130 millimeters.

#### Example 14

1.575 parts of the zinc chloride double salt of the diazonium chloride derived from 3-nitro-4-amino anisole is dissolved in 21.5 parts of water containing 0.23 part of diallylamine hydrochloride. The resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. The resulting printing paste is suited for the production of fast Bordeaux prints upon cotton cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. The printing paste so prepared retains its relative viscosity, and hence its utility for printing, much better than a similar paste prepared in exactly the same manner but without the diallylamine hydrochloride. This advantage is shown in the following table:

Printing paste used	Relative viscosity reading after 2 min.	Relative viscosity reading after 2 hours
Containing diallylamine hydrochloride.....	53.6	20.0
Without diallylamine hydrochloride.....	45.6	1.3

These relative viscosity readings are the times in seconds for copper plated steel shot weighing approximately 0.107 gram each to fall 130 millimeters.

#### Example 15

1.57 parts of the zinc chloride double salt of the diazonium chloride of 3-nitro-4-amino anisole, and 0.446 part of tetra-allyl ammonium bromide are dissolved in 21 parts of water and the resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. The resulting printing paste is used for the production of fast Bordeaux prints upon cotton cloth impregnated with arylides of 2-hydroxy-3-naphthoic acid.

In a similar manner, 1.63 parts of the zinc chloride double salt of the diazonium chloride of 2,5-dichloroaniline is mixed with 0.46 parts of tetra allyl ammonium bromide and the resulting mixture is dissolved in 21 parts of water. This solution is then intimately mixed with 75 parts of 2.5% carob bean gum to form a printing paste which is eminently suited for the production of bright scarlet prints upon cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid.

The advantages that these printing pastes possess over similarly prepared pastes not containing tetra allyl ammonium bromide, are shown in the following table:

Diazotized amine in printing paste	Thinning inhibitor in printing paste	Relative viscosity reading after 2 min.	Relative viscosity reading after 3 hours
3-nitro-4-amino anisole.....	Tetra-allyl ammonium bromide.....	69.5	48.2
Do.....	None.....	62.4	1.3
2, 5-dichloro aniline.....	Tetra-allyl ammonium bromide.....	96.8	90.3
Do.....	None.....	83.3	19.0

These relative viscosity measurements are the times in seconds for copper plated steel shot weighing approximately 0.107 gram each to fall 130 millimeters.

#### Example 16

1.575 parts of the zinc chloride double salt of the diazonium chloride derived from 3-nitro-4-amino anisole and 0.34 part N-allyl-N,N-dimethyl-N-phenyl ammonium chloride are dissolved in 24 parts of water, and the resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. The resulting printing paste is suitable for the preparation of fast Bordeaux prints on cotton cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. This printing paste retains its relative viscosity and, hence, its usefulness for printing, much better than a similar paste which does not contain the allyl dimethyl phenyl ammonium chloride, as is shown in the following table:

Printing paste used	Relative viscosity reading after 2 to 4 min.	Relative viscosity reading after 2 hours
Containing thinning inhibitor.....	44.6	25.4
Without thinning inhibitor.....	45.0	1.0

These relative viscosity readings are the times in seconds for copper plated steel shot weighing approximately 0.107 gram each to fall 130 millimeters.

#### Example 17

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 a strength of 15.35% real base, are dissolved in 21 parts of water along with 0.20 part of N-allyl urea. The resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. The resulting printing paste is valuable for the preparation of fast Bordeaux prints upon cotton cloth impregnated with arylides of 2-hydroxy-3-naphthoic acid, and is superior to a similar paste which does not contain the allyl urea because of the fact that it retains its relative viscosity and, hence, its utility for printing much better. This advantage is shown in the following table:

Printing paste used	Relative viscosity reading after 2 min.	Relative viscosity reading after 2 hours
Containing allyl urea.....	39.6	18.6
Without allyl urea.....	40.1	1.4

These relative viscosity measurements are the times in seconds for copper plated steel shot weighing approximately 0.107 gram each to fall 130 millimeters.



## Example 18

Printing pastes are made in the following manner:

An amount of the zinc chloride double salt of the diazonium (or tetrazonium) chloride derived from an ice color base equal to 0.005 equivalent parts is mixed with 0.512 parts of allyl guanidine sulfate and the mixture is dissolved in enough water to make 25 parts of solution. The resulting solution is intimately mixed with 75 parts of 2.5% carob bean gum. These printing pastes are used for the preparation of fast color prints upon cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. These printing pastes retain their relative viscosity and hence their utility to the printer, very much better than similar pastes similarly prepared but without the allyl guanidine sulfate. This advantage may be seen by consulting the following table:

Base used for zinc chloride double salt	Thinning inhibitor in printing paste	Relative viscosity measurement after 2 min.	Relative viscosity measurement after 4 hrs.	Color of print on anilide of 2-hydroxy-3-naphthoic acid
2,5-dichlor aniline.....	Allyl guanidine sulfate..	66.8	66.0	Yellowish scarlet.
Do.....	None.....	61.2	10.2	Do.
4-nitro-2-amino anisole.....	Allyl guanidine sulfate..	69.4	65.6	Reddish scarlet.
Do.....	None.....	76.2	13.2	Do.
3-nitro-4-amino anisole.....	Allyl guanidine sulfate..	85.6	40.0	Bordeaux.
Do.....	None.....	83.2	0.4	Do.
Ortho dianisidine.....	Allyl guanidine sulfate..	66.4	49.6	Navy blue.
Do.....	None.....	71.4	9.2	Do.

These relative viscosity measurements are the times in seconds for copper plated steel shot weighing 0.107 gram each to fall 130 millimeters.

This application is in part a continuation of our co-pending application, Serial No. 437,201, filed April 1, 1942.

We claim:

1. 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 an organic compound with not more than sixteen carbon atoms selected from the group of organic nitrogenous bases soluble in aqueous mineral acids and containing at least one olefinic double bond for twelve carbon atoms, organic nitrogenous bases soluble in aqueous mineral acids containing at least one acetylenic triple bond for twelve carbon atoms, and water soluble salts of the above bases, this compound being free from constituents capable of azoic coupling, of forming diazo amino or diazo imino compounds under acid conditions, of catalytically decomposing diazonium salts at room temperature, this compound being also free from primary and secondary amino groups if used together with amines before diazotization, the amount of the nitrogenous base being sufficient to substantially inhibit thinning of a carbohydrate thickener.

2. A printing paste containing a carbohydrate thickener, at least one water soluble diazonium salt derived from an ice color diazo component and an organic compound having not more than 16 carbon atoms belonging to the group consist-

ing of organic nitrogenous bases soluble in aqueous mineral acids and containing at least one olefinic double bond for 12 carbon atoms, organic nitrogenous bases soluble in aqueous mineral acids containing at least one acetylenic triple bond for 12 carbon atoms, and water soluble salts of the above bases, this compound being free from constituents capable of azoic coupling, of condensation with the diazonium salt to form diazo-amino or diazoimino compounds under acid conditions, or catalytically decomposing the diazonium salt at room temperature, the amount of the nitrogenous base present being sufficient to substantially inhibit thinning of the carbohydrate thickener.

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

4. A composition according to claim 2 in which

the diazonium salt is a diazonium chloride-zinc chloride double salt.

5. A composition according to claim 1 in which the nitrogenous base is an allylguanidine.

6. A composition according to claim 2 in which the nitrogenous base is an allylguanidine.

7. A composition according to claim 1 in which the nitrogenous compound is a tetra-allylammonium compound.

8. A composition according to claim 2 in which the nitrogenous compound is a tetra-allylammonium compound.

9. A composition comprising water soluble diazonium salts derived from an ice color diazo component and an organic compound with not more than 16 carbon atoms selected from the group consisting of organic nitrogenous bases soluble in aqueous mineral acids and containing at least one olefinic double bond for 12 carbon atoms, organic nitrogenous bases soluble in aqueous mineral acids containing at least one acetylenic triple bond for twelve carbon atoms, and water soluble salts of the above bases, this compound being free from constituents capable of azoic coupling, of forming diazo amino or diazo imino compounds under acid conditions and of catalytically decomposing diazonium salts at room temperature, the amount of the nitrogenous base being sufficient to substantially inhibit thinning of a carbohydrate thickener.

10. A composition according to claim 1 in which the nitrogenous compound is an allyl urea.

11. A composition according to claim 2 in which the nitrogenous compound is an allyl urea.

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