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PREVENTION OF THINNING OF CARBOHYDRATE PRINTING PASTES CONTAINING DIAZONIUM SALTS WITH OLEFIN CARBOXYLIC ACID AMIDES

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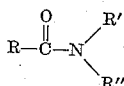
11 Claims. (Cl. 8-71)

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This invention relates to new compositions containing certain ice color forming components such as diazo components or diazonium salts and certain ingredients capable of inhibiting the thinning of carbohydrate thickened printing pastes prepared from these compositions. More specifically, it relates to compositions containing as thinning inhibitors olefin carboxylic acid amides.

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 subsequently printing upon these goods with a printing paste containing a diazonium salt derived from an ice color diazo component. The diazonium salt is either prepared in solution before use by diazotizing the corresponding amine base, or it is applied in the form of a stable diazonium salt. This well known and cheap process is open to a very serious disadvantage. The printing pastes containing the diazonium salt and a carbohydrate thickener tend to thin out rapidly, losing their desired printing consistency. It is with the prevention of this thinning action that the present invention is concerned.

According to the present invention, 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 are associated with a water-soluble olefin carboxylic acid amide, represented by the formula:



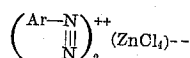
wherein R is an alkenyl radical containing not more than four carbon atoms; R' and R'' are radicals selected from the group consisting of hydrogen, alkyl, omega-hydroxyalkyl and alkenyl radicals containing not more than four carbon atoms.

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



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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 acids 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 explosibility; 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 sometimes being 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:



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 iso-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 which 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 the same 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 and the present invention does not deal with any other types of paste. 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.

Further evidence appears to indicate 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 quantity of azo dyestuff obtained indicated that the bulk of the diazonium salt was undecomposed while the filtrate still showed the reaction of starch and not the reaction of reducing sugars.

The degree of thinning action differs widely and depends upon the structure of the diazo component from which the diazonium salt is derived. We have found that those diazonium salts that are known to be very active couplers in the production of azo dyestuffs are also the worst thinners, while those that are slow in coupling power generally thin to a much lesser degree. Although there is certainly some parallelism in the coupling power and thinning action, these two properties are not strictly proportionate. The diazonium salts that are derived from nitranilines 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 derived from ortho-nitranilines thin more than those derived from the meta and para compounds. On the other hand, the diazonium salts derived from the 2-methyl-4-chloroaniline and from ortho-anisidine have only little thinning action. Obviously, the rate of 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 as thickeners and their viscosity is equally influenced by diazonium salts. It will be noted that all 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.

According to the present invention the thinning action of the diazonium salts on the carbohydrate printing pastes is inhibited or greatly reduced by using water soluble olefin carboxylic acid amides. While not critical the effective concentration of the thinning inhibitors of the present invention will vary to a considerable degree with the particular diazonium compound present in the paste and with the particular thinning inhibitors. In general, from 20 to 50% of thinning inhibitor based on the total weight of the particular amine from which the diazonium compound is produced give optimum results. With certain exceptional diazonium compounds amounts of thinning inhibitor below 20% are effective, and in certain other cases amounts above 50% may be used with advantage.

The olefin carboxylic acid amides must contain at least one double bond. They may contain more than one and the nitrogen of the amide may carry one or two alkenyl groups.

Some typical examples of olefin carboxylic acid amides useful in the present invention are: propenoic acid amide (acrylamide), propenoic acid-N-(omega-hydroxy methyl) amide (methylol acrylamide), 2-methyl propenoic acid amide (methyl acrylamide or methacrylamide), Δ^2 -butenoic acid amide (crotonamide), Δ^2 -butenoic acid-N-allylamide (N-allyl crotonamide), Δ^2 -butenoic acid-N,N-diallyl amide (N,N-diallyl crotonamide), Δ^2 -butenoic-N-ethylamide (N-ethyl crotonamide), 3-methyl- Δ^2 -butenoic acid amide (dimethyl-acrylamide), Δ^3 -butenoic acid amide (vinyl acetamide), Δ^2 -pentenoic acid amide (beta-ethyl acrylamide), Δ^4 -pentenoic acid amide (allyl acetamide), 2-methyl- Δ^2 -butenoic acid amide (tiglic acid amide), and the like.

Preparation of these new thinning inhibitors in most cases is accomplished by the customary procedure of reacting the olefin carboxylic acid halide with ammonia or an amine, though in some specific cases preparation is best accomplished through dehalogenation of the corresponding dibromo or dichloro derivative or by dehydrohalogenation of the corresponding mono-bromo or mono-chloro derivative of the saturated amide.

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:

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, 2,5-difluoroaniline, 2-fluoro-5-chloroaniline, 2,5-dichloroaniline, m-amino-benzotrifluoride, 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 nitro-anilines, 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-

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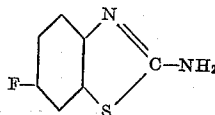
naphthylamine, 2-amino-diphenylether, 2-amino-4-acetyl-diphenylether, benzyl-2-aminophenylether, 3-fluoro-4-methoxyaniline, 2-methoxy-5-chloroaniline, 2,5-dimethoxy-4-chloroaniline, 2-methoxy-4-chloro-5-methylaniline, 2-methoxy-5-bromoaniline, 3-bromo-6-ethoxy-aniline, 4-chloro-2-amino-diphenylether, 4-amino-2-chloro-diphenylether, 4-amino-4'-chloro-diphenylether, 4,4'-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-toluylenediamine, N-benzoyl-p-phenylene diamine; monoacyl derivatives of diamino-phenol ethers, as e. g., 2-benzoyl-amino-4-aminoanisole, 2-hexahydrobenzoyl-amino-5-aminoanisole, 2-amino-5-benzoyl-amino-hydroquinone dimethyl ether and diethylether, 2-amino-5-hexahydrobenzoyl-amino-hydroquinone dimethylether and diethylether, 2-amino-5-butyrylamino-hydroquinone dimethylether and diethylether, 2-amino-5-phenoxyacetyl-amino-hydroquinone diethylether, the monomethyl and the monobenzyl and the monophenylurethane 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 dimethyl-sulfonamide and diethylsulfonamide, 3-amino-4-methoxy-benzene diethylsulfonamide; xenylamine; alpha and beta naphthylamine; alpha aminoanthraquinone; 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-aminodiphenylamine, 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 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 2,6-dichloro-1,4-phenylene diamine. Diazonium salts deriving from diamines in which both amino groups are diazotized

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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.

Diazonium salts derived from heterocyclic amines or diamines fall also 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-nitro-benzothiothiophene, 1-amino-5-fluorobenzothiazole:



The method of addition of the thinning inhibitor is not critical. In general it may be added in various stages in the production of the diazonium printing paste. Thus, the aromatic amines used in forming ice color diazo compounds may be blended with the inhibitor and the blends then diazotized in the customary manner and incorporated into a printing paste. Another method is to blend diazotizable amine salts with the inhibitor, which gives the same result on diazotization. A further variant is to dissolve the inhibitor and the base separately before diazotization. A second general procedure is to blend the inhibitor with diazonium salts which are very stable per se, or which may have been stabilized by conventional means. The blend forms a solid composition which can be incorporated into a printing paste. A variant of the second procedure is to add the inhibitor to a prepared diazo solution before the printing paste is made up. The fact that the introduction of the thinner can be effected in so many ways imparts a desirable flexibility to the present invention, which is a practical working advantage.

The above methods of introducing the thinning inhibitor are preferred. However, the invention is not limited thereto. In a number of cases it is possible to mix the diazonium salt with the printing gum and add the inhibitor afterwards. This procedure, however, is not universally applicable with full effectiveness because in the case of very active diazo compounds a certain amount of thinning may take place before the inhibitor is added. This somewhat restricts the scope of this modification, which should normally be used only with diazo compounds which do not thin carbohydrates at an excessive rate. With many printing pastes containing diazonium compounds, however, this procedure is effective and is included within the broad scope of the present invention.

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

Example 1

329 parts of the dry mixture of the zinc chloride double salt of the diazonium chloride derived from 4-methyl-2-nitroaniline and a sufficient quantity of partially dehydrated aluminum sulfate and anhydrous magnesium sulfate to reduce the strength to 23.1% on an amine basis are intimately mixed with 21.6 parts of acrylamide and 81.4 parts of partially dehydrated aluminum sulfate. This mixture is then dissolved in 2500 parts of water, and the resulting solution is in-

imately mixed with 7500 parts of 2.5% aqueous carob bean gum.

381 parts of the dry mixture of the zinc chloride double salt of the diazonium chloride derived from 4-chloro-2-nitroaniline and sufficient partially dehydrated aluminum sulfate to reduce the strength to 22.6% on an amine basis are intimately mixed with 23.2 parts of acrylamide, the resulting mixture is dissolved in 2500 parts of water, and the solution so obtained is intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

288 parts of a dry mixture of the zinc chloride

pastes have the outstanding advantage over similar pastes which do not contain acrylamide in that their relative viscosities and hence their utility for textile printing are maintained much longer than the relative viscosities of similar pastes which do not contain this amide. This advantage of the pastes containing the acrylamide over those which do not is shown in the following table. In this table the relative viscosities shown are the times in seconds for copper plated steel shot weighing 0.358 gram apiece to fall through 130 mm. of the printing paste in a glass tube of 20 mm. diameter.

Thinning Inhibitor used	Base Used for Diazonium Salt	Relative Viscosity 2 min. After Mixing	Relative Viscosity 1 Hr. After Mixing	Relative Viscosity 3 Hrs. After Mixing	Color of Print on Anilide of 2,3-Hydroxy-Naphthoic Acid
Acrylamide	4-methyl-2-nitro aniline	29.5	26.5	21.0	Bluish red.
None	do.	23.5	2.5	Less than 0.5	Do.
Acrylamide	4-chloro-2-nitro aniline	29.8	27.0	22.0	Yellowish red.
None	do.	24.5	2.0	Less than 0.5	Do.
Acrylamide	2-methoxy-5-nitro aniline	48.0	45.0	44.0	Reddish scarlet.
None	do.	42.5	12.5	6.0	Do.
Acrylamide	2,5-dichloro aniline	48.5	38.0	40.0	Yellowish scarlet.
None	do.	34.5	1.5	Less than 0.5	Do.
Acrylamide	Ortho dianisidine	26.0	22.5	16.0	Navy blue.
None	do.	25.5	3.5	Less than 0.5	Do.
Acrylamide	4-methoxy-2-nitro aniline	28.0	23.5	16.5	Bordeaux.
None	do.	25.5	0.5	Less than 0.5	Do.

Example 2

double salt of the diazonium chloride derived from 2-methoxy-5-nitroaniline and sufficient anhydrous magnesium sulfate and partially dehydrated aluminum sulfate to reduce the strength to 29.1% on an amine basis, are intimately mixed with 32.8 parts of acrylamide and 116.2 parts of anhydrous magnesium sulfate. The resulting dry powder is dissolved in 2500 parts of water, and the solution so obtained is intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

394 parts of the dry mixture of the zinc chloride double salt of the diazonium chloride derived from 2,5-dichloro aniline and sufficient partially dehydrated aluminum sulfate to reduce the strength to 20.55% on an amine basis are thoroughly mixed with 20.9 parts of acrylamide. The resulting dry powder is then dissolved in 2500 parts of water, and the solution thus prepared is intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

320 parts of the dry mixture of the zinc chloride double salt of the tetrazonium chloride derived from ortho-dianisidine and sufficient anhydrous magnesium sulfate to reduce the strength to 19.1% on an amine basis are intimately mixed with 19.3 parts of acrylamide and 37 parts of anhydrous sodium sulfate. The resulting mixture is then dissolved in 2500 parts of water, and the solution so made is thoroughly and intimately mixed with 7500 parts of 2.5% aqueous carob gum.

343 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-methoxy-2-nitroaniline and sufficient anhydrous magnesium sulfate to reduce the strength to 24.5% on an amine basis are mixed with 34 parts of acrylamide and 77 parts of anhydrous sodium sulfate. The resulting dry mixture is then dissolved in 2500 parts of water, and the solution so obtained is thoroughly mixed with 7500 parts of 2.5% aqueous carob bean gum.

The six printing pastes described above are useful for the preparation of fast color prints on cloth impregnated with ice color coupling components, such as the anilide of 2,3-hydroxy-naphthoic acid. Furthermore, these printing

2000 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-methyl-2-nitroaniline and sufficient anhydrous magnesium sulfate and partially dehydrated aluminum sulfate to reduce the strength to 17.6% on an amine basis are intimately mixed with 102.5 parts of methacrylamide (melting point 111°-112° C.). 363 parts of this mixture, which contains 4.7% by weight of methacrylamide, are dissolved in 2500 parts of water, and the resulting solution is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

343 parts of mixture of the zinc chloride double salt of the diazonium chloride derived from 4-methoxy-2-nitroaniline and sufficient anhydrous magnesium sulfate to reduce the strength to 24.5% on an amine basis are mixed with 34 parts of methacrylamide and 77 parts of anhydrous sodium sulfate. The resulting mixture is then dissolved in 2500 parts of water and the resulting solution is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

381 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-chloro-2-nitroaniline and sufficient partially dehydrated aluminum sulfate to reduce the strength to 22.6% on an amine basis are intimately mixed with 23.2 parts of methacrylamide, and the resulting mixture is dissolved in 2500 parts of water. The solution thus made is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

The three printing pastes described above are useful for the preparation of bright fast color prints on cloth impregnated with ice color components, such as, for example, the anilide of 2,3-hydroxy-naphthoic acid. These pastes, containing methacrylamide, retain their viscosity, and hence their usefulness for printing, a much longer time than similar pastes prepared without the use of methacrylamide. This advantage is clearly shown in the following table. In this table, the relative viscosity figures are the times for stainless steel spheres weighing 1.023 grams apiece or lead spheres weighing 0.536 gram apiece

to fall through 130 mm. of the paste in a tube 20 mm. in diameter.

from 4-methoxy-2-nitroaniline and sufficient anhydrous magnesium sulfate to reduce the strength

Thinning Inhibitor Used	Based Used for Diazonium Salt	Kind of Sphere for Relative Viscosity Measurement	Relative Viscosity 3 Min. After Mixing	Relative Viscosity 1 Hr. After Mixing	Relative Viscosity 3 Hrs. After Mixing	Color of Print on Anilide of 2,3-Hydroxy-Naphthoic Acid
Methacrylamide.....	4-methyl-2-nitro aniline.....	stainless steel	16.0	16.0	14.5.....	bluish red.
None.....	do.....	do.....	13.5	2.0	Less than 0.5.....	Do.
Methacrylamide.....	4-methoxy-2-nitroaniline.....	Lead	18.0	17.5	16.0.....	Bordeaux.
None.....	do.....	do.....	16.0	0.5	Less than 0.5.....	Do.
Methacrylamide.....	4-chloro-2-nitro aniline.....	do.....	14.0	14.0	12.5.....	yellowish red.
None.....	do.....	do.....	12.5	2.0	Less than 0.5.....	Do.

Example 3

329 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-methyl-2-nitroaniline and sufficient partially dehydrated aluminum sulfate and anhydrous magnesium sulfate to reduce the strength to 23.1% on an amine basis are mixed with 81.4 parts of partially dehydrated aluminum sulfate and the resulting mixture is dissolved in 2450 parts of water. To this solution is then added 60 parts of a 36% aqueous solution of N-methylol acrylamide and the resulting solution is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

381 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-chloro-2-nitroaniline and sufficient partially dehydrated aluminum sulfate to reduce the strength to 22.6% on an amine basis are dissolved in 2440 parts of water to which are then added 60 parts of a 36% aqueous solution of N-methylol acrylamide. The resulting solution is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

These printing pastes described above are used for the production of fast color prints on fabrics impregnated with ice color coupling components

15 to 24.5% on an amine basis are mixed with 34 parts of crotonamide and 77 parts of anhydrous sodium sulfate. The resulting mixture is dissolved in 2500 parts of water, and the solution thus obtained is intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

20 381 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-chloro-2-nitroaniline and sufficient partially dehydrated aluminum sulfate to reduce the strength to 22.6% on an amine basis are mixed with 23.2 parts of crotonamide. The resulting mixture is dissolved in 2500 parts of water, and the solution so obtained is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

30 The two printing pastes described above are useful for the preparation of fast color prints on material impregnated with the usual ice color components such as the anilide of 2,3-hydroxy-naphthoic acid. These printing pastes retain their body or viscosity much better than similar pastes made in the same manner but without crotonamide. This is shown in the following table. In this table the relative viscosities are the times in seconds for lead spheres weighing 0.536 gram apiece to fall through 130 mm. of the paste in a tube 20 mm. in diameter.

Thinning Inhibitor	Base Used for Diazonium salt	Relative Viscosity 3 Min. After Mixing	Relative Viscosity 1 Hr. After Mixing	Relative Viscosity 3 Hrs. after Mixing	Shade of Print on Anilide of 2,3-Hydroxy-naphthoic acid
Crotonamide.....	4-methoxy-2-nitroaniline.....	19.5	9.5	5.0.....	Bordeaux.
None.....	do.....	16.0	0.5	Less than 0.5.....	Do.
Crotonamide.....	4-chloro-2-nitroaniline.....	13.5	8.0	3.0.....	yellowish red.
None.....	do.....	12.5	2.0	Less than 0.5.....	Do.

such as, for example, the anilide of 2,3-hydroxy-naphthoic acid. These printing pastes maintain their viscosity, and hence are useful for the preparation of prints, for a much longer time than pastes similarly made but without the N-methylol acrylamide. This is shown in the following table.

In this table, the figures for the relative viscosities are the times in seconds for copper plated steel shot weighing 0.358 gram apiece to fall through 130 mm. of the paste in a tube 20 mm. in diameter.

Thinning Inhibitor	Base Used for Diazonium Salt	Relative Viscosity 2 Mins. After Mixing	Relative Viscosity 1 hr. After Mixing	Relative Viscosity 3 Hrs. After Mixing	Color of Print on Anilide of 2,3-Hydroxy-Naphthoic Acid
N-methylol acrylamide.....	4-methyl-2-nitroaniline.....	28.5	25.0	22.5.....	bluish red.
None.....	do.....	23.5	2.5	Less than 0.5.....	Do.
N-methylol acrylamide.....	4-chloro-2-nitroaniline.....	30.5	25.0	21.5.....	yellowish red.
None.....	do.....	24.5	2.0	Less than 0.5.....	Do.

Example 4

343 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived

dry powder is dissolved in 2500 parts of water. There is then dissolved in this solution 34 parts of N-allyl crotonamide and the resulting solution

55 The crotonamide used in this example melted at 159°-160° C. and was prepared from crotonyl chloride and liquid ammonia according to the method of Stoermer et al., Ber. 47, 1789 (1914).

Example 5

343 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-methoxy-2-nitroaniline and sufficient anhydrous magnesium sulfate to reduce the strength to 24.5% on an amine basis are mixed with 77 parts of anhydrous sodium sulfate and the resulting

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is intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

Another printing paste is made in exactly the same manner except that the N-allyl crotonamide is omitted.

The printing pastes prepared as described above are used for the preparation of fast color prints on material impregnated with ice color coupling components such as the anilide of 2,3-hydroxynaphthoic acid. The former printing paste, containing the N-allyl crotonamide, maintains its viscosity, and hence its utility for printing, much longer than the latter paste which does not contain this amide. This difference is shown in the following table, in which the relative viscosity figures are the times in seconds for lead shot weighing on an average of 0.5365 gram apiece to fall through 130 mm. of the paste in a tube 20 mm. in diameter.

The N-allyl crotonamide is prepared by allowing one molecular proportion of crotonyl chloride to react in ether solution with approximately 3 molecular proportions of allyl-amine. The allyl-amine hydrochloride formed during the reaction is filtered off, and the excess allylamine and ether are evaporated from the filtrate, leaving the desired N-allyl crotonamide as a viscous oil.

	Paste Containing N-Allyl Crotonamide	Paste Containing No Thinning Inhibitor
Relative viscosity:		
3 mins. after mixing.....	17.5	16.0
15 mins. after mixing.....	17.5	5.5
1 1/2 hr. after mixing.....	17.5	2.0
1 hr. after mixing.....	15.5	0.5
2 hrs. after mixing.....	12.0	Less than 0.5

Example 6

381 parts of a mixture of the zinc chloride double salt of the diazonium chloride derived from 4-chloro-2-nitroaniline and sufficient partially dehydrated aluminum sulfate to reduce the strength to 22.6% on an amine basis are dissolved in 2500 parts of water and to the solution are then added 23.2 parts of N-ethyl crotonamide. The resulting solution is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

Another printing paste is prepared in exactly the same manner except that no N-ethyl crotonamide is used in its preparation. These pastes are suited for the preparation of fast red prints on material impregnated with the usual ice color coupling components, for example, the anilide of 2,3-hydroxynaphthoic acid, but the former paste, containing the N-ethyl crotonamide maintains its viscosity longer, and hence can be used by the printer for a longer time than the latter which does not contain this N-ethyl crotonamide. This difference is shown by the figures in the following table, in which the relative viscosity figures are the times in seconds for spherical lead shot weighing on an average 0.5365 gram apiece to fall through 130 mm. of the paste in a tube 20 mm. in diameter.

The N-ethyl crotonamide is prepared from crotonyl chloride and anhydrous ethylamine in ether solution by the same procedure as that described in Example 5 for the preparation of N-allyl crotonamide. The N-ethyl crotonamide thus prepared is a pale yellowish oil.

	Paste Containing N-ethyl Crotonamide	Paste Containing No Thinning Inhibitor
Relative Viscosity:		
3 mins. after mixing.....	13.0	12.5
15 mins. after mixing.....	12.5	6.5
30 mins. after mixing.....	10.5	4.5
45 mins. after mixing.....	10.0	3.5
1 hr. after mixing.....	8.0	2.0
1.5 hrs. after mixing.....	6.0	0.5

Example 7

200 parts of 4-methoxy-2-nitroaniline, 50 parts of acrylamide and 150 parts of sodium chloride are thoroughly ground together in a mortar to form a homogeneous orange powder. This mixture can be used for the preparation of a printing paste which retains its viscosity, and hence its utility for printing, a much longer time than a printing paste made from the same base but without the acrylamide. This is shown by the following illustration:

168 parts of the mixture of 4-methoxy-2-nitroaniline, acrylamide and salt described above is thoroughly mixed with 1000 parts of water and 325 parts of 5N hydrochloric acid and sufficient ice to lower the temperature to approximately 5° C. To the resulting slurry is then added over a period of two or three minutes 550 parts of 1N sodium nitrite solution and the resulting mixture is stirred until diazotization is complete, 15 or 20 minutes being sufficient. The resulting diazo solution is then filtered to remove small amounts of impurity and diluted with water until it occupies the same volume as 2500 parts of water. This solution is then intimately mixed with 7500 parts of 2.5% aqueous carob bean gum.

Another printing paste is then made in exactly the same manner except that 84 parts of 4-methoxy-2-nitroaniline are substituted for 168 parts of the mixture of base, acrylamide and salt. The superiority of the paste made from the base containing the acrylamide is shown in the following table, in which the relative viscosity figures are the times in seconds for spherical lead shot weighing on an average 0.5365 gram apiece to fall 130 mm. through the paste in a tube 20 mm. in diameter.

Thinning Inhibitor in Printing Paste	Acrylamide	None
Relative viscosity:		
2 mins. after mixing.....	15.0	14.0
0.5 hr. after mixing.....	13.5	6.5
1 hr. after mixing.....	11.5	4.0
1.5 hr. after mixing.....	10.0	3.0
3 hrs. after mixing.....	9.0	1.5

Example 8

A thorough mixture is made in a mortar of the following ingredients:

	Parts
2-methoxy-4-nitroaniline.....	200
Methacrylamide (M. P. 111-112° C.).....	50
Epsom salts.....	150

168 parts of the mixture described above is intimately mixed with 1000 parts of water and 320 parts of 5N hydrochloric acid and enough ice to reduce the temperature to approximately 10° C. To this mixture is then quickly added 550 parts of 1N sodium nitrite solution and the resulting mixture is stirred for about half an hour, filtered and the filtrate is diluted with water to the volume occupied by 2500 parts of water. This solution is

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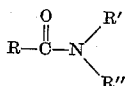
then mixed with 7500 parts of 2.5% aqueous carob bean gum.

In an entirely similar manner another printing paste is prepared from 84 parts of 2-methoxy-4-nitroaniline alone. These two printing pastes are used for the production of fast prints on the fiber impregnated with ice color coupling components, for example, for the production of fast bluish red prints on cloth padded with an alkaline solution of the anilide of 2,3-hydroxy-naphthoic acid. The former paste, however, which contains the methacrylamide, maintains its viscosity much longer than the other and hence is useful for printing for a longer period of time. This is illustrated by the following figures, in which the relative viscosities are the times in seconds for lead shot weighing on an average 0.5365 gram apiece to fall 130 mm. through the paste in a tube 20 mm. in diameter.

Thinning Inhibitor Used in Printing Paste	Methacrylamide	None
Relative Viscosity:		
2 mins. after mixing	15.0	15.0
0.5 hr. after mixing	14.0	9.5
1 hr. after mixing	12.5	7.0
1.5 hrs. after mixing	11.5	5.5
2 hrs. after mixing	11.0	5.0
3 hrs. after mixing	11.0	4.0

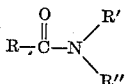
We claim:

1. A composition suitable for the preparation of printing pastes containing carbohydrate 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 associated therewith an olefin carboxylic acid amide represented by the following formula:



wherein R is an alkenyl radical containing not more than four carbon atoms, R' and R'' are radicals selected from the group consisting of hydrogen, alkyl, omega-hydroxyalkyl and alkenyl radicals containing not more than four carbon atoms; the amount of organic olefin carboxylic acid amide being sufficient to substantially inhibit thinning of a carbohydrate thickener.

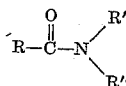
2. A composition suitable for the preparation of printing pastes containing carbohydrate thickeners comprising an ice color-forming component included in the group of water-soluble diazonium salts; the color-forming component having associated therewith an olefin carboxylic acid amide represented by the following formula:



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wherein R is an alkenyl radical containing not more than four carbon atoms, R' and R'' are radicals selected from the group consisting of hydrogen, alkyl, omega-hydroxyalkyl and alkenyl radicals containing not more than four carbon atoms; the amount of olefin carboxylic acid amide being sufficient to substantially inhibit thinning of a carbohydrate thickener.

3. A printing paste containing a carbohydrate thickener, at least one water-soluble diazonium salt derived from an ice color diazo component, and an olefin carboxylic acid amide represented by the following formula:



wherein R is an alkenyl radical containing not more than four carbon atoms, R' and R'' are radicals selected from the group consisting of hydrogen, alkyl, omega-hydroxyalkyl and alkenyl radicals containing not more than four carbon atoms, the amount of olefin carboxylic acid amide being sufficient to substantially inhibit thinning of the carbohydrate thickener.

4. A composition according to claim 1 in which the olefin carboxylic acid amide is propenoic acid amide.

5. A composition according to claim 2 in which the olefin carboxylic acid amide is propenoic acid amide.

6. A composition according to claim 3 in which the olefin carboxylic acid amide is propenoic acid amide.

7. A composition according to claim 1 in which the olefin carboxylic acid amide is 2-methyl propenoic acid amide.

8. A composition according to claim 2 in which the olefin carboxylic acid amide is 2-methyl propenoic acid amide.

9. A composition according to claim 3 in which the olefin carboxylic acid amide is 2-methyl propenoic acid amide.

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

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

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