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2,953,422

## STABLE SOLUTION FOR PRODUCING ICE COLORS

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No Drawing. Filed Dec. 31, 1956, Ser. No. 631,426

13 Claims. (Cl. 8-45)

This invention relates to the production of solutions of ice color compositions and more particularly to the provision of stable aqueous solutions suitable for producing ice colors on the fiber.

In the azoic dyeing and printing of fibrous materials such as textile fibers, leather and the like, a diazotizable aromatic or heterocyclic primary amine, usually called the azoic diazo base, devoid of water-solubilizing groups such as carboxylic and sulfonic acid groups, is diazotized and coupled on the fiber with an azoic coupling component, also devoid of solubilizing groups. The diazo may be in the form of a freshly prepared diazo or as a pre-stabilized diazo. In some cases wherein the diazonium salt is relatively stable, it may be as the sulfate or chloride, but more often it is stabilized as a double salt with a compound such as zinc chloride, or as a diazoamino compound with a stabilizing amine.

The stabilizing amines are primary, or more preferably, secondary amines; they may be alkyl, aryl or heterocyclic; they contain solubilizing groups which solubilize the diazoamino compound, such as sulfonic, carboxylic, polyoxy and the like groups, and at least one replaceable hydrogen atom attached to an amino nitrogen atom.

One usual method of producing fabrics colored with azoic dyes is to print the material with an alkaline paste which consists of both the diazoamine and the coupler and then develop the color in situ by treatment with a weak acid, in some few cases with steam, but preferably with acidified steam.

A representative composition which comprises a diazoamino compound and an azoic coupler is available on the market under the trademark "Rapidogen" (General Aniline & Film Corp.), and such term, as used herein, is used in reference to this type of composition.

For the most part Rapidogens have been produced and sold in powder form. However, recently there has been interest in Rapidogens in solution form.

Such stabilized ice color solutions are, however, subject to certain objections. Over extended periods of time in storage, the diazo compound decomposes somewhat with evolution of nitrogen so that there is a danger of pressure developing in the container. Furthermore, premature formation of the dye by coupling may occur which leads to turbid solutions or the formation of a sediment. This is not only detrimental from an esthetic sense but causes difficulty in handling, since the liquor must be free of sediment in order to give level dyeings. Further, as a result of this deterioration, the intensity of the color developed on the fiber is reduced, and duller dyeings are obtained. This tendency towards deterioration is particularly serious in the case of such solutions formulated to produce blue and violet dyeings, the tendency being aggravated by higher temperatures prevalent in various locations and seasons.

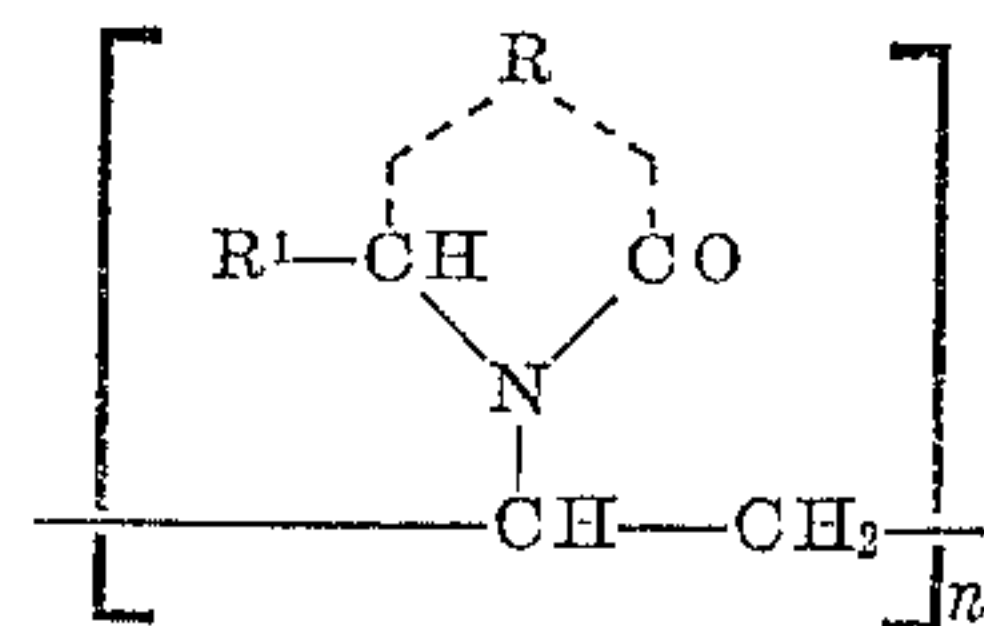
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It is an object of this invention to provide an aqueous alkaline solution suitable for producing ice colors on the fiber which will not be subject to the above disadvantages. Another object of this invention is the provision of a stable aqueous alkaline solution containing an ice color diazo compound stabilized and solubilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom, and an ice color coupling component. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which includes an aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom, an ice color coupling component, and about 0.5 to 5% by weight of a water-soluble polymeric material containing at least about 20% by weight of a polymerized N-vinyl lactam. It has been found that the above-defined compositions of the instant invention are surprisingly stable and resistant to sedimentation and deterioration even at elevated temperatures up to 120° F. or more. The mechanism by which these improved and unexpected results are attained is not fully understood, although it is probable that some sort of complex formation occurs since polymerized N-vinyl lactams are known to form complexes with a great many compounds.

The water-soluble polymer employed in the instant invention may be a homo-polymer of an N-vinyl lactam, a copolymer of an N-vinyl lactam and one or more other polymerizable monomers, or a mixture of a polymerized N-vinyl lactam and at least one other polymer, it being understood that in the case of copolymers and mixtures of polymers, there must be present at least about 20% by weight of a polymerized N-vinyl lactam.

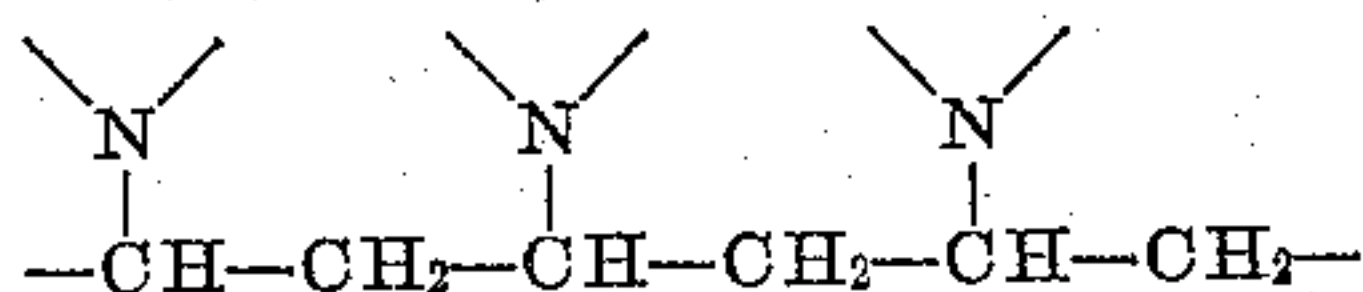
Polymeric N-vinyl lactams, as exemplified by polyvinylpyrrolidone (PVP, poly-1-vinyl-2-pyrrolidone, poly-N-vinyl-2-pyrrolidone, poly-N-vinyl- $\alpha$ -pyrrolidone), are by this time well known as extremely versatile chemicals which have found many uses in a variety of fields. They are white powders or colorless, horn-like or glass-like materials with a high softening point and have the highly desirable property of being soluble in water. They are characterized by the following recurring structural formula:



wherein R represents an alkylene bridge group e.g. ethylene, propylene, butylene, necessary to complete a 5, 6 or 7-membered heterocyclic ring system; R<sup>1</sup> represents hydrogen or a lower alkyl group such as methyl or ethyl; and n represents a number indicative of the extent of polymerization and is usually at least about 25. They are obtained by polymerizing organic 5, 6, or 7-membered ring compounds containing in their rings the —NH—CO— group such as, for example, N-vinyl-2-pyrrolidone, N-vinyl-5, -4, and -3-methyl-2-pyrrolidones, N-vinyl-3,3-dimethyl-2-pyrrolidone, N-vinyl- $\epsilon$ -caprolactam, N-vinyl-



hexahydrophthalimidine and the like. Depending upon the extent of polymerization, they may have molecular weights ranging from at least about 5,000 up to 80,000 or more, and preferably from about 25,000 to about 40,000. Viscosity measurements are commonly used as an indication of the average molecular weight of polymeric compositions, the instant polymers being characterized by a chain of carbon atoms to which the lactam rings are attached through their nitrogen atoms, as follows:



The K value (Fikentscher) of any particular mixture of polymers is calculated from viscosity data and is useful as an indication of the average molecular weight of such mixture. Its determination is fully described in "Modern Plastics," 23, No. 3, 157-61, 212, 214, 216, 218 (1945) and is defined as 1000 times  $k$  in the empirical relative viscosity equation:

$$\frac{\log_{10} \eta_{rel}}{C} = \frac{75k^2}{1 + 1.5kC} + k$$

wherein  $C$  is the concentration in grams per hundred cc. of polymer solution and  $\eta_{rel}$  is the ratio of the viscosity of the solution to that of pure solvent. The K values are reported as 1000 times the calculated viscosity coefficient in order to avoid the use of decimals. For the purpose of the present invention, there may be employed those polymeric N-vinyl lactams having a K value of about 10 to 200, and preferably of about 15 to 100.

K values and specific viscosities ( $\eta_{sp}$ ) are interconvertible and are related through relative viscosity ( $\eta_{rel}$ ). Thus, when viscosity measurements are taken on solutions which have a concentration of 1.00 gram of polymer per deciliter of solution at 25° C. ( $C=1$ ), the relationships are as follows:

$$\eta_{rel} = \eta_{sp} + 1$$

Relative viscosity = specific viscosity plus one.

$$\text{Relative viscosity} = 10^{[0.001K + 0.000075K^2 / (1 + 0.0015K)]}$$

Hence,

$$\eta_{sp} = -1 + 10^{[0.001K + 0.000075K^2 / (1 + 0.0015K)]}$$

dimensionless, whereas inherent viscosity

$$\frac{(\log_e \eta_{rel})}{C}$$

and intrinsic viscosity (the limit of inherent viscosity as  $C$  approaches zero) have the dimensions of dilution, i.e., the reciprocal of concentration. Intrinsic viscosity and K are intended to be independent of concentration.

The number of recurring polymer units enclosed by brackets in the foregoing general structural formula, indicated by "n," or the extent or degree of polymerization, corresponds to a chain of roughly 25 to 1,000 monomer units or more. In actual practice, a mixture of polymeric molecules, each containing a different number ( $n$ ) of monomer units, is always produced. These homopolymers are readily prepared by the procedural steps given in U.S. Patents 2,265,450, 2,317,804 and 2,335,454 in which working examples of species included within the above formula are given and which are incorporated herein by reference thereto.

Water-soluble copolymers operative in the instant invention are derived from polymerizable monomeric compositions containing at least about 20% by weight of an N-vinyl lactam. The proportion of N-vinyl lactam present in such polymerizable monomeric compositions will depend upon the amount and nature of the other monomer or monomers, but should in all cases be at least sufficient to impart to the final copolymer the desired water soluble property. By way of example, the following list gives the maximum limit of representative monomers

which may be copolymerized with the N-vinyl lactam for the production of operable copolymers:

	Percent
Allyl alcohol	50
5 Diallyl phthalate	20
Isobutyl vinyl ether	20
Ethyl vinyl ether	50
Methyl vinyl ether	80
Maleic anhydride	80
10 Vinyl acetate	40
Vinyl chloride	35
Acrylic acid	75
Vinyl laurate	20
Vinyl stearate	15

15 The following table lists some monomeric compositions useful in the production of suitable water-soluble copolymers.

TABLE

	Percent
20 N-vinyl-2-pyrrolidone	70
+	
Allyl alcohol	30
N-vinyl-2-pyrrolidone	85
25 +	
Diallyl phthalate	15
N-vinyl-2-pyrrolidone	60
+	
Vinyl ethyl ether	40
30 N-vinyl-2-pyrrolidone	30
+	
Vinyl methyl ether	70
N-vinyl-2-pyrrolidone	75
35 +	
Vinyl acetate	25
N-vinyl-2-pyrrolidone	50
+	
40 Acrylic acid	50
N-vinyl-2-pyrrolidone	20
+	
Maleic anhydride	80
N-vinyl-2-pyrrolidone	94
45 +	
Vinyl stearate	6
3-methyl-N-vinyl-2-pyrrolidone	87
+	
50 Vinyl bromide	13
3-methyl-N-vinyl-2-pyrrolidone	87
+	
Vinyl chloride	13
55 4-methyl-N-vinyl-2-pyrrolidone	88
+	
Vinyl chloride	12
3,3-dimethyl-N-vinyl-2-pyrrolidone	91
+	
60 Vinyl chloride	9

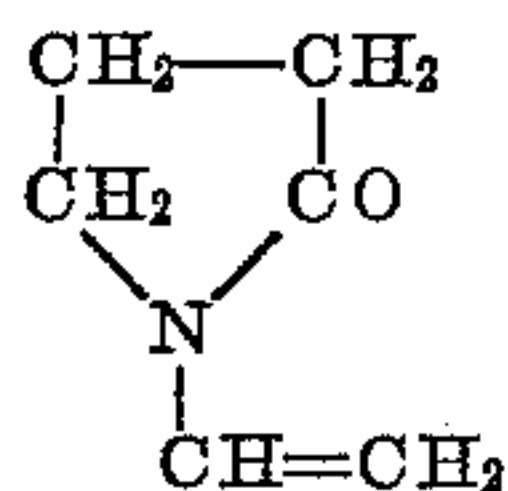
It will be understood that the above-described copolymers are generally prepared in the same manner as the homopolymers of the N-vinyl lactams and have similar properties with respect to water-solubility, K values and the like.

Instead of copolymers prepared from mixtures of monomers as described above, a water-soluble polymeric material may be employed which is produced by mixing the polymerized N-vinyl lactam with one or more of the polymerized monomeric unsaturated compounds employed in producing such copolymers provided of course that the mixture contains at least 20% of polymerized N-vinyl lactam, is water soluble, and has the above-described properties with respect to K values and the like.



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The preferred N-vinyl lactams for use in the compositions of the instant invention are N-vinyl-2-pyrrolidone and its lower alkyl substituted derivatives, which may be characterized by the formula:



in which one or more of the hydrogen atoms in the cyclic methylene groups may be substituted by the lower alkyl radical such as methyl, ethyl or the like.

The ice color diazo components operative in the compositions of the instant invention are well known in the art and in general include diazotizable primary amine compounds devoid of solubilizing groups such as carboxylic or sulfonic acid groups. Included among such compounds are such aromatic and heterocyclic amines as anilines, xenylamines, naphthylamines, benzidines, aminocarbazoles, aminofuranes, aminothiazoles, aminoarylsulfones, aminodiphenyl ethers, aminobenzophenones, aminofluorenones, aminoazo compounds, and the like. As specific examples of some suitable ice color diazo components, there may be mentioned aminoazo toluene, 4-chloro-2-nitroaniline, 5-chloro-o-toluidine, 4-nitro-o-toluidine, 2,5-dichloroaniline, 4-benzamido-2,5-diethoxyaniline, 4-amino-m-anisidine, 4-nitro-o-anisidine, 4-chloro-o-anisidine, 1-aminonaphthalene, 1-aminanthraquinone, dianisidine, 5-chloro-4-nitro-o-anisidine, aminobenzophenone, aminodiphenylsulfone, 2,6-dichloro-1,4-phenylenediamine, benzidine, 4,4'-diaminostilbene, and the like.

Prior to incorporation in the solutions of the instant invention, the ice color diazo component is diazotized in known manner as by treatment with sodium nitrite and dilute hydrochloric acid, and the resulting ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side in known manner by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom. The resulting stabilized ice color diazo compounds are often referred to as diazoamino, diazoimino, and diazoamidino compounds and the like, and generically under the term diazoamino compounds. The organic amines employed for such stabilization are well known and are reacted with the ice color diazo compound in proportions sufficient to react with all the diazo groups therein. As representative of such stabilizing organic amines, there may be mentioned by way of example, N-methyl taurine, sarcosine, 4-sulfo-2-aminobenzoic acid, 5-sulfo-2-methylaminobenzoic acid, 5-sulfo-2-ethylaminobenzoic acid, 1-aminobenzoic-3,6-disulfonic acid,  $\alpha$ -naphthylamine-2,4-disulfonic acid,  $\beta$ -naphthylamine-4,6,8-trisulfonic acid, proline, pyrrolidine- $\alpha$ -sulfonic acid, glucamine, methyl glucamine, guanyl urea-N-sulfonic acid, guanyl taurine, N-nitroguanyl urea, 2-biguanidyl naphthalene-1-sulfonic acid, creatine cyanamide, and the like. Carboxylic and sulfonic acid groups are preferred as the solubilizing groups, but other groups are known such as ammonium salt groups and polyalcohol radicals and the like.

In general, the stabilized ice color diazo compounds employed in the solutions of the instant invention are formed by the reaction of the diazo derivative of a strongly basic diazotizable primary amine with a stabilizing amine of weak basicity. Such stabilized compounds do not undergo a coupling reaction in alkaline media in the presence of an ice color coupling component, but in the presence of acidic reagents, they split, permitting coupling of the ice color diazo compound with the ice color coupling component.

The ice color coupling components operative in the instant invention, also well known in the art, are devoid of solubilizing groups such as carboxylic or sulfonic acid groups. In general, these coupling components may be

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characterized as compounds having an active methylene group, an enolizable keto group or an aromatic hydroxy group inducing coupling, usually in ortho- or para-position, preferably the former, to said hydroxy group. Such

5 compounds are typified by the acylacetarilides (e.g. anilides, etc.), the pyrazolones, and aromatic hydroxy compounds capable of coupling. As acylacetarilides there may be mentioned acetoacetic acid arylides, furoyl acetic acid arylides, terephthaloyl-bis-acetic acid arylides, and the like. As pyrazolones, there may be mentioned 1-phenyl-3-methyl-5-pyrazolone, 1-p-tolyl-3-methyl-5-pyrazolone, 3-methyl-5-pyrazolone, 5-pyrazolone, 1,3-dimethyl-5-pyrazolone, 1-(p-chlorophenyl)-3-methyl-5-pyrazolone, 1-(p-nitrophenyl)-3-methyl-5-pyrazolone, 1-(o-methoxyphenyl)-3-methyl-5-pyrazolone, 1-(m-aminophenyl)-3-methyl-5-pyrazolone, 1-methyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone-3-carboxylic acid methyl ester, 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester, and other 5-pyrazolones either unsubstituted or substituted in the 1- and/or 3-positions by non-solubilizing radicals. The aromatic (carbocyclic or heterocyclic) hydroxy compounds useful as coupling components therein generally include phenols, resorcinols, 1- and 2-naphthols, benzonaphthols, hydroxy-benzofluorenones, hydroxyazo compounds such as (o-hydroxyaniline  $\rightarrow$  resorcinol) coppered and aniline  $\rightarrow$  8-amino-2-naphthol and the like, in addition to arylides of  $\beta$ -hydroxy aromatic and heterocyclic carboxylic acids. Illustratively, examples of such arylides (e.g. anilides, etc.) which may be employed in the process of the instant invention are 3-hydroxy-2-naphthoic acid arylides, 3-hydroxy-2-anthraic acid arylides, 3-hydroxy-2-carbazole carboxylic acid arylides, 3-hydroxy-2-furane carboxylic acid arylides, 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid arylides, hydroxydibenzothiophene carboxylic acid arylides and the like. These and other such ice color coupling components operative herein are disclosed in Diserens, "Chemical Technology of Dyeing and Printing," volume 1, pages 213 to 224 (Reinhold Publishing Corp., 1948); Lubs, "Chemistry of Synthetic Dyes and Pigments," pages 182 through 192 (Reinhold Publishing Corp., 1955); and Adams, "Journal of the Society of Dyers and Colorists," volume 67 (1951), beginning at page 223.

The solutions of the instant invention should contain in known manner approximately equivalent proportions of the stabilized ice color diazo component and ice color coupling component whereby substantially no unreacted components remain after coupling has taken place on the fiber. The instant solutions are preferably of concentrations near the saturation point and usually contain from about 10 to 25% by weight of the Rapidogen (combined weight of stabilized diazo compound and coupling component). As stated above, improved and unexpected results of the instant invention are attained by incorporating into these solutions about 0.5 to 5% by weight of the above-described water soluble polymeric material containing at least about 20% by weight of a polymerized N-vinyl lactam and more preferably a water soluble homo-polymer of N-vinyl-2-pyrrolidone. The stabilized solutions of the instant invention are employed for the azoic dyeing of fibrous materials in known manner and there is accordingly no need to further describe their manner of application.

The solutions of the instant invention may be prepared in any desired manner and the components mixed in any desired order. It is preferred, however, to employ an auxiliary organic solvent solution concentration of about 5 to 50% by weight to assist in solubilizing the components of the solution, such solvent being usually an alcohol such as ethylene glycol, diethylene glycol, propylene glycol and 1,4-butanediol, and their methyl, ethyl, propyl, and butyl ethers, methanol, ethanol, propanol, butanol, cyclohexanol, and mixtures thereof and the



like. Generally the stabilized ice color diazo compound and the ice color coupling component are added to an aqueous alkaline solution containing the organic solvent, the said water-soluble polymeric material added, and an additional amount of water then added to yield a clear stable solution. If desired, known assistants, thickening agents, dispersing agents and the like may be included. The pH of the instant solutions should be more than 7 and preferably about 9 to 13.

The following examples, in which parts are by weight unless otherwise indicated, are illustrative of the instant invention and are not to be regarded as limitative.

#### Example 1

16 g. benzamidocresidine, diazotized and stabilized with sarcosine, 12 g. 3-hydroxy-2-naphthanilide and 1.4 g. 3-hydroxy-2-naphth-o-toluidide are added to a mixture of 40 g. Cellosolve, 100 g. water and 6.2 g. KOH at a temperature below 40° C. and stirred to solution. 10 g. poly-N-vinyl-2-pyrrolidone (K=30) are then added. The solution is then made up to 200 g. with water, stirred to solution and filtered.

A control solution is made up in similar manner, but excluding the polyvinylpyrrolidone.

These solutions are placed in an oven at 120° F. in closed containers. After 2 weeks, the control solution contains considerable sediment and gives dyeings that are 5% weaker than the original solution whereas the other solution is still clear at the end of 6 months, and prints full strength.

#### Example 2

10.5 g. 4'-amino-2',5' - diethoxybenzanilide, diazotized and stabilized with N-methyltaurine, 6.1 g. dianisidine, tetrazotized and stabilized with N-methyltaurine and 18.8 g. 3-hydroxy-2-naphth-o-toluidide are added to a mixture of 30 g. Cellosolve, 10 g. diethyleneglycol and 7 g. KOH. To this is added 2 g. poly-N-vinyl-2-pyrrolidone (K=26) and the solution made up to 200 g. After stirring to solution, the solution is filtered.

At the end of 3 months storage at 110° F. this solution shows no signs of sedimentation whereas a control, made up without the polyvinylpyrrolidone, shows signs of sedimentation after 1½ weeks.

#### Example 3

20.8 g. dianisidine, tetrazotized and stabilized with N-methyl taurine and 20.8 g. 3-hydroxy-2-naphth-o-toluidide are mixed into 27 g. Cellosolve, 9 g. diethyleneglycol and 11.8 g. KOH at a temperature below 40° C. To this is added 1 g. poly-N-vinyl-2-pyrrolidone (K=30). The solution is made up to 200 g. with water, stirred to solution and filtered.

At the end of three months storage at 110° F. this solution shows no signs of sedimentation whereas a control, made without the polyvinylpyrrolidone, contains sediment after 2 weeks.

#### Example 4

A solution is made up as described in Example 3 above using:

11.6 g. 4'-amino-2',5'-diethoxybenzanilide, diazotized and stabilized with N-methyltaurine,  
7.3 g. 4'-amino-2',5'-dimethoxy-benzanilide, diazotized and stabilized with N-methyltaurine,  
13.4 g. 3-hydroxy-2-naphthoic acid  $\alpha$ -naphthalide,  
45 g. Cellosolve,  
15 g. diethyleneglycol,  
6.5 g. KOH, and  
3 g. polyvinylpyrrolidone (K=30) made up to 200 g. with water.

A storage test of this solution in comparison to a control which does not contain polyvinylpyrrolidone shows this solution to be much more stable.

#### Example 5

131 g. diazoamino from 2,5-dichloroaniline diazotized and stabilized with 5-sulfo-2-ethylaminobenzoic acid is added to a mixture of 100 g. Cellosolve, 50 g. diethylene glycol, 200 g. water and 31 g. solid KOH. 96 g. 3-hydroxy-2-naphth-o-phenetidine is added, together with 30 g. PVP (K=40). The weight is made up to 1,000 g. with water. The solution shows no sedimentation after an extended period in storage.

#### Example 6

45 g. diazoamino from 3-amino-N,N-dimethyl-p-toluene-sulfonamide diazotized and stabilized with 5-sulfo-2-methylamino-benzoic acid is added to a mixture of 100 g. water, 75 g. Cellosolve, 25 g. diethylene glycol and 20 g. KOH. 20.2 g. 3-hydroxy-2-naphth-1,3-xylylidide and 10.2 g. 3-hydroxy-2-naphth-m-nitro-anilide are added. 10 g. PVP (K=35) is then added, and the weight made up to 500 g. The solution shows no sedimentation after an extended period in storage.

#### Example 7

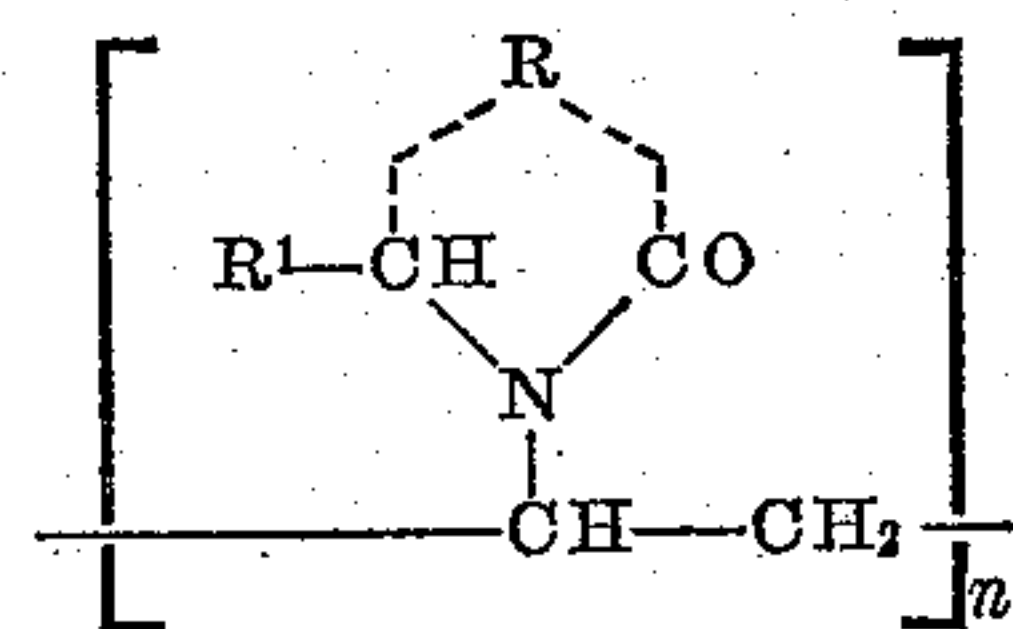
20 parts of the Rapidogen solution produced in Example 1 is mixed with 15 parts caustic soda 40° Bé. and pasted with 65 parts neutral starch tragacanth.

Cotton cloth is printed with this paste by means of a roller and color developed by passing through a chamber containing steam acidified with acetic and formic acid vapors for 2-4 minutes. A violet print is produced.

This invention has been disclosed with respect to certain preferred embodiments, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

We claim:

1. An aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least 1 solubilizing group and at least 1 replaceable hydrogen atom attached to an amino nitrogen atom, an ice color coupling component, and about 0.5 to 5% by weight of a water-soluble polymeric material containing at least about 20% by weight of a polymerized N-vinyl lactam having a K value of about 10 to 200 and characterized by the formula



wherein R represents a lower alkylene group necessary to complete a 5 to 7 membered heterocycle; R<sup>1</sup> is selected from the group consisting of hydrogen and lower alkyl; and n represents a number indicative of the extent of polymerization.

2. A solution as defined in claim 1 in which said water-soluble polymeric material is a homo-polymer of an N-vinyl lactam.

3. A solution as defined in claim 1 in which said water-soluble polymeric material is polymerized N-vinyl-2-pyrrolidone.

4. A solution as defined in claim 1 in which said organic amine is sarcosine.

5. A solution as defined in claim 1 wherein said organic amine is N-methyl taurine.

6. A solution as defined in claim 1 in which said organic amine is 4-sulfo-2-aminobenzoic acid.

7. A solution as defined in claim 1 in which said organic amine is 5-sulfo-2-ethylaminobenzoic acid.

8. A solution as defined in claim 1 in which said organic amine is 5-sulfo-2-methylaminobenzoic acid.



9. An aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with sarcosine, an ice color coupling component, and about 0.5 to 5% by weight of a water-soluble polymer of N-vinyl-2-pyrrolidone having a K value of about 10 to 200.

10. An aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with N-methyltaurine, an ice color coupling component, and about 0.5 to 5% by weight of a water-soluble polymer of N-vinyl-2-pyrrolidone having a K value of about 10 to 200.

11. An aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with 4-sulfo-2-aminobenzoic acid, an ice color coupling component, and about 0.5 to 5% by weight of a water-soluble polymer of N-vinyl-2-pyrrolidone having a K value of about 10 to 200.

12. An aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with 5-sulfo-2-ethyl-aminobenzoic acid, an ice color coupling component, and about 0.5 to 5% by weight of a water-

soluble polymer of N-vinyl-2-pyrrolidone having a K value of about 10 to 200.

13. An aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with 5-sulfo-2-methyl-aminobenzoic acid, an ice color coupling component, and about 0.5 to 5% by weight of a water-soluble polymer of N-vinyl-2-pyrrolidone having a K value of about 10 to 200.

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