This invention relates to the dyeing of textile fibers and is directed more particularly to improvements in the art of fugitively tinting such fibers, both natural and synthetic. A prior application is a continuation-in-part of my prior application, Serial No. 380,587, filed September 16, 1953.

For many years, a considerable variety of fugitive tints, the so-called "sighting" colors, have been used for tinting such fibers as viscose and acetate rayon. These tints are useful in identifying various lots of fibers during the processes of carding, roving, spinning, weaving, and the like, and serve to avoid the mixing of different lots of fibers during processing into finished fabric form. In the past, most fugitive tints have been selected from the acid dye class. With some care in the selection process, it is not difficult to find a full range of colors which are quite fugitive from cellulose or cellulose esters.

Recently, however, the textile industry has been faced with the necessity of identifying a much larger variety of fibers than heretofore, and acid dyestuffs have been found quite unsatisfactory in most cases for the tinting of synthetic fibers other than those derived from cellulose. Up to the present time, the search among commercial dyestuffs for fugitive tints for the fibers produced from polyacrylonitrile or copolymers of acrylonitrile and other vinyl monomers (Orlon, Acrilan, Creslan, and Dynel), or from polyamides (nylon and Perlon) has been notably unsuccessful.

In order to properly fulfill their function, tints must be readily removable from the fabric by simple scouring during the first stages of finishing; the problem in tinting most synthetic fibers lies in the fact that practically all commercial dyes stain these fibers and cannot be removed by simple scouring. The problem is greatly aggravated when several fibers of different chemical types are blended to improve various physical properties, such as crease-resistance, of the finished textile. In such instances, it is practically impossible to find, among commercial dyes, even a single color which is satisfactorily fugitive from all components of the blend. In the past, such blends have, for the most part, been processed without tinting, and substantial losses to the mill have occurred in cases where lots become mixed. Steaming, which is frequently employed to reduce kinkiness in high twist yarns, often sets an otherwise fugitive tint on the fiber and renders it difficult, or even impossible, to remove during the finishing process. Stripping of tints can sometimes be accomplished by the finisher, but this procedure is likely to damage the cloth and, at best, adds to the cost of the finishing.

I have found that by selection of dyestuffs with due regard for their chemical structure and incorporation of these with certain water-soluble synthetic polymers, fugitive tints can be formulated which will scour readily from woven or knitted textiles of practically any composition under very mild conditions. In some cases, rinsing in cold water alone is sufficient to effect complete removal. The polymers which I employ in practicing my invention inhibit diffusion of certain dyes into the fiber, even in the presence of heat and moisture, rendering them much more readily removable during scouring than they would be in the absence of the polymer. During scouring, the mixture of dyestuff and synthetic resin dissolves and diffuses readily to the surface of the textile structure, from which it is carried away completely by the scouring bath, leaving a colorless substrate which may subsequently be dyed in any desired shade.

The polymers which I have found most effective in promoting fugitivity are poly-N-vinyl lactams, such as poly-N-vinyl butyrolactam and poly-N-vinyl caprolactam. Poly-N-vinyl butyrolactam, commonly known as polyvinylpyrrolidone (PVP), is commercially available in a wide range of molecular weights. I have found that the effect of polymer molecular weight on fugitivity is not large. Molecular weight is ordinarily defined in terms of \( K^* \) values, and polymers having \( K^* \) values in the range of 15 to 20, for example, have been used successfully in the practice of this invention. From a practical standpoint, it is generally desirable to use polymers of relatively low molecular weight.

I prefer to incorporate in the tint formulation at least about 50 percent of polymeric material based on the dry weight of the dyestuff used, and, depending somewhat on the severity of steaming to which the tinted fibers are to be subjected, the required concentration of polymeric material may vary up to 500 to 1,000 percent or higher based on the dyestuff weight.

The use of PVP-dye combinations as fugitive tints has already been suggested in the literature. Earlier investigators, however, have confined their studies to dyes of the direct class. Although it is true that some direct dyes in combination with PVP do have some utility as fugitive tints, colors of this type are far less versatile than the products contemplated by the present invention. I have found, quite unexpectedly, that colored watersoluble metal chelates in combination with poly-N-vinyl lactams are far more fugitive than any tints known heretofore. On the basis of this observation, it has been possible to develop a considerable range of colored tints, not previously available as commercial colors, which are particularly well suited for use in fugitive tinting. These dyes, and an improved method of preparing them, are described in detail in my copending application, Serial No. 533,242, filed September 6, 1955. As the chelate dyestuffs normally, i.e., in the absence of a poly-N-vinyl lactam, have a strong affinity for most, if not all, of the various textile fibers currently available, it is particularly surprising that they are suitable for use as the tinctorial constituent of a fugitive tint which must necessarily be free of such affinity.

The metal chelates which are most useful in the practice of this invention are aromatic compounds having chromophoric and auxochromic groups in which the metal atom is held in a 5- or 6-membered ring, on one side by a normal covalent bond and on the other by a coordinate link.

In most cases, water solubility is achieved in these chelates by the introduction of sulfonic, carboxylic, or hydroxyl groupings (other than those which are part of the chelate ring). The presence of additional groups of this type is not necessary for attaining water solubility in all chelates, however; the ferrous chelates of 2,2'-bipyridine and 1,10-phenanthroline, for example, are not soluble.
water soluble, and contain none of the common hydrophilic substituents. Typical of the groupings which can form such chelates are the following:

<table>
<thead>
<tr>
<th>Class</th>
<th>Groupings</th>
<th>Typical Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>N=O</td>
<td>1. nitroso-2-naphthol-6-sulfonic acid, sodium salt (Nitroso Schaefer's salt).</td>
</tr>
<tr>
<td>2.</td>
<td>C-OH</td>
<td>2. nitroso-1-naphthol-4-sulfonic acid, sodium salt (Nitroso Neville and Winnie's salt).</td>
</tr>
<tr>
<td>3.</td>
<td>C-OH</td>
<td>4,7-dihydroxynaphthalene-2-sulfonic acid, sodium salt.</td>
</tr>
<tr>
<td>4.</td>
<td>C-OH</td>
<td>1,8-dihydroxynaphthalene-3,6-sulfonic acid (Chromotropic acid).</td>
</tr>
<tr>
<td>5.</td>
<td>C-OH</td>
<td>5-hydroxy-2-(hydroxymethyl) -4-pyrene (Rochelle).</td>
</tr>
<tr>
<td>6.</td>
<td>C-OH</td>
<td>1,2-dihydroxyanthraquinone-3-sulfonic acid sodium salt (Alizarine Red B, Color Index 1084).</td>
</tr>
<tr>
<td>7.</td>
<td>C-OH</td>
<td>2,5'-dipyridine, 1,10-phenanthroline.</td>
</tr>
</tbody>
</table>

The above list of groupings is by no means all-inclusive, and it will be obvious to those skilled in the art that there are quite a variety of additional ones which also give rise to colored chelates useful in the practice of my invention.

The effectiveness of the chelate-poly-N-vinyl lactam combination as a fugitive tint depends to some extent on the structure of the compound used for chelation. Thus, because I have found that they are generally more fugitive from fibers of widely varying chemical type, and because of their lower cost, I prefer to use compounds containing groups of the types listed in classes 1 through 4 above. Compounds of classes 5 and 6 form chelates which are also useful as tints, but are somewhat more limited in their application.

It is of some importance in obtaining maximum fugitivity to maintain as low a concentration as possible of inorganic salts in the poly-N-vinyl lactam chelate mixture. Halides, such as common salt, are particularly undesirable.

Tinting mixtures of the water-soluble synthetic resins and metal chelate dyestuffs may be prepared as powders, solutions, or pastes. They may be incorporated, moreover, in marking crayons; in this form they are equally effective for identifying textile products or other materials, and such markings are as readily removed from the substrate as the color applied from water solution by the usual tinting methods.

It is sometimes advantageous to plasticize the polymer to prevent its drying to a hard brittle solid before the tint can be distributed uniformly over the fiber mass. Compounds such as glycerol, ethylene glycol, polyethylene glycols, and similar materials are useful for this purpose. In general, I prefer to incorporate from about 10 percent to 400 percent of plasticizer based on the resin weight. In cases where the use of such materials is indicated, plasticizers have been found to be most desirable in cases where the tinting solution is applied to the stock as a liquid stream. In cases where the tint is applied by spraying the use of plasticizers is generally less important.

To more clearly define my invention, without limiting its scope, the following illustrative examples are given:

**Example I**

A tinting solution containing Naphthol Green B, Color Index Number 5, the iron chelate of nitroso Schaefer's salt, was prepared according to the formula given below:

<table>
<thead>
<tr>
<th>Component:</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthol Green B</td>
<td>0.5</td>
</tr>
<tr>
<td>Poly-N-vinyl pyrrolidone, K-30</td>
<td>3.0</td>
</tr>
<tr>
<td>Water</td>
<td>100.0</td>
</tr>
</tbody>
</table>

This solution was applied by spraying to wool top, Type 41 and Type 42 Orion staple, acrylic fibers supplied by the du Pont Company, Acrilan staple, an acrylic fiber supplied by the Chemstrand Corporation; nylon and Perlon polyamide staple fibers; viscose rayon staple, acetate rayon staple; and Dacron polyester staple supplied by the du Pont Company, following which the samples were air dried and steamed at 160° Fahrenheit dry bulb and 150° Fahrenheit wet bulb for one hour. After steaming, the tinted fibers were scoured for ten minutes in a solution containing 0.1 percent of alkyl aryl sulfonate detergent at 120° Fahrenheit. The color was readily removed leaving the fibers substantially white, whereas identical distributions of fibers similarly treated with a solution which did not contain polyvinyl-pyrrolidone could not be scoured free of the dyestuff.

**Example II**

A tinting solution containing Naphthol Green B, Color Index Number 5, the iron chelate of nitroso Schaefer's salt, was prepared according to the formula given below:

<table>
<thead>
<tr>
<th>Component:</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthol Green B</td>
<td>0.5</td>
</tr>
<tr>
<td>Poly-N-vinyl caprolactam, K-30</td>
<td>3.0</td>
</tr>
<tr>
<td>Water</td>
<td>100.0</td>
</tr>
</tbody>
</table>

This solution was applied by spraying to wool top; Type 41 and Type 42 Orion staple, acrylic fibers supplied by the du Pont Company; Acrilan staple, an acrylic fiber supplied by the Chemstrand Corporation; nylon and Perlon polyamide staple fibers; viscose rayon staple, acetate rayon staple; and Dacron polyester staple supplied by the du Pont Company, following which the samples were air dried and steamed at 160° Fahrenheit dry bulb and 150° Fahrenheit wet bulb for one hour. After steaming, the tinted fibers were scoured for ten minutes in a solution containing 0.1 percent of alkyl aryl sulfonate detergent at 120° Fahrenheit. The color was readily removed, leaving the fibers substantially white, whereas identical distributions of fibers similarly treated with a solution which did not contain poly-N-vinyl caprolactam could not be scoured free of the dyestuff.

**Example III**

The cobalt chelate of 2-nitroso-1-naphthol-4-sulfonic acid, sodium salt, a red dye, was prepared according to the following formula:

<table>
<thead>
<tr>
<th>Component:</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-naphthol-4-sulfonic acid, sodium salt</td>
<td>22.8</td>
</tr>
<tr>
<td>CoSO₄.7H₂O</td>
<td>7.5</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>4.0</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>7.0</td>
</tr>
<tr>
<td>Water</td>
<td>250.0</td>
</tr>
</tbody>
</table>

The naphthol sulfonic salt and the cobalt sulfate were dissolved in the water at 175° F., the sulfuric acid was added with stirring, and the sodium nitrite, dissolved in twice its weight of water, was added at such a rate that the loss of oxygen from the solution was in appreciable. After addition of the nitrite, the solution
2,959,481 was neutralized to pH 7.0 with sodium bicarbonate, and filtered. The red dye solution was evaporated, yielding 29 parts of dry color.

A tinting powder was prepared from the above color by intimately blending the following ingredients:

Component: Parts by weight
Cobalt chelate of 2-nitroso-1-naphthol-4-sulfonic acid, sodium salt .................................................. 5
Polyvinylpyrrolidone, K-90 ................................................................. 12

This mixture was dissolved in 50 parts of water to produce a compound paste. When the paste was further diluted with 200 parts of water, it was a relatively thin liquid, which was then applied by spraying to samples of those fibers listed in Example I. When steamed and scoured in accordance with the procedure of this example, the color was completely removed. A similar set of samples, treated with dye solution containing no PVP, was deeply stained, and the color could not be removed, even by scouring at boiling temperature.

**Example IV**

The nickel chelate of 2-nitroso-1-naphthol-5-sulfonic acid, sodium salt, an orange dye, was prepared as follows:

Component: Parts by weight
1-naphthol-5-sulfonic acid, sodium salt (L salt) .................................................. 22.8
NiSO₄·7H₂O ................................................................. 7.5
H₂SO₄ ................................................................. 4.0
NaNO₃ ................................................................. 7.0
Water ................................................................. 250.0

The naphth sulfonic acid and the nickel sulfate were dissolved in the water at 85° F., the sulfuric acid was added with stirring, and the sodium nitrate, dissolved in twice its weight in water, was added at such a rate that the loss of oxides of nitrogen from the solution was appreciable. The orange dye formed precipitated in plates, and was separated from the mother liquor, after neutralization to pH 7.0 with sodium bicarbonate, by filtration. The dye was dried in vacuum at 105° F.; the yield was 30 parts of dry color.

A tinting solution was prepared from the above dye according to the following formula:

Component: Parts by weight
Dye ........................................................................ 5
Pereg ST, a 30 percent water solution of polyvinylpyrrolidone, approximately K-30 supplied by the Dow Chemical Company ........................................... 36
Water ...................................................................... 59

This solution was applied by hand blending to the fibers listed in Example I in the amount of one percent based on the dry fiber weight. When steamed and scoured as in Example I, the color was completely removed from the fibers, whereas a similar dye solution containing no PVP produced severe staining.

**Example V**

The titanium chelate of 6,7-dihydroxy naphthlene-2-sulfonic acid was prepared by dissolving together 10 parts of this compound with 6 parts of commercial titanyl sulfate of the approximate formula Ti(SO₄)₂·9H₂O in 500 parts of water at room temperature. The brown solution resulting was neutralized with ammonium hydroxide to pH 8, whereupon it became a bright lemon yellow. The dye was filtered to remove traces of titanyl dioxide, following which 30 parts of poly-N-vinylpyrrolidone, K-12, and 90 parts of a commercial polyethylene glycol, having an average molecular weight of 600, were dissolved in it.

Approximately two percent by weight of this concentrated tinting solution was applied in droplets to samples of the fibers listed in Example I and uniformly distributed over the stock by hand blending. The samples were steamed and scoured as in Example I, and the color was found to be completely removed. Application of a similar dye solution containing no polymer produced a deep stain which could not be removed by scouring.

**Example VI**

The iron chelate of sodium catechol disulfonate was prepared as follows:

Component: Parts by weight
1,2-dihydroxy benzene-3,5-disulfonic acid, sodium salt .................................................. 3.8
FeSO₄·9H₂O ................................................................. 1.8
Water ...................................................................... 94.4

The sodium catechol disulfonate was dissolved in the water, at room temperature, and the ferric sulfate was added, with stirring. The solution became an intense blue, and after 5 minutes the pH was adjusted to 8.0 with ammonium hydroxide. The color changed to bright red upon neutralization. This dye solution was filtered to remove a small amount of precipitated ferric hydroxide.

A tinting solution was prepared by dissolving 10 parts of K-30 poly-N-vinylpyrrolidone in the filtered dye solution. This tint was applied to fiber samples and steamed as in Example I. It was completely removed by simple scouring, in contrast with a similar solution containing no PVP, which stained the fibers and could not be scoured from them.

**Example VII**

The titanium chelate of chromotropic acid was prepared according to the procedure outlined in Example V; 8 parts of chromotropic acid were substituted for the 10 parts of 6,7-dihydroxy naphthlene-2-sulfonic acid, sodium salt, used in Example V. The chelate is a reddish yellow.

A tinting solution was prepared by dissolving 4 parts of poly-N-vinylpyrrolidone, having a K value of 40, in the dye solution. This solution, when applied to the fibers listed in Example I and tested similarly, was found to be completely fugitive.

**Example VIII**

An orange dye was prepared as follows:

Component: Parts by weight
Kojic acid ........................................................................ 5.0
FeSO₄·9H₂O ................................................................. 4.9
Water ...................................................................... 200.0

The kojic acid and ferrous sulfate were each dissolved in 100 parts of water, and were then stirred together at room temperature. The deep red solution resulting was changed to a bright orange color on neutralization with sodium bicarbonate to pH 7. After filtering to remove insoluble material, 12 parts of poly-N-vinylpyrrolidone having a K value of 20 were dissolved in the dye solution. When checked by the procedure of Example I, this tint was found to be fugitive from all of the fibers listed in that example.

**Example IX**

A red tinting solution was prepared from the following materials:

Component: Parts by weight
1,2-dihydroxy anthraquinone-3-sulfonic acid, sodium salt (Alizarine Red S, Color Index Number 1034) ........................................................................................................ 3.0
Al₂(SO₄)₃·18H₂O ................................................................. 1.0
Poly-N-vinylpyrrolidone, K-30 ................................................................. 12.0
Water ...................................................................... 100.0

The dye, aluminum sulfate, and polymer were dissolved together in the water at 120° F., and the solution pH was adjusted to 8.0 with ammonium hydroxide. After cooling to room temperature the intense red tint was
applied by hand blending to the fibers listed in Example I. The tint was readily scoured from the fibers after steaming for one hour, whereas a similar tint containing no PVP could not be scoured from an otherwise identical lot of fibers.

Example X

The red tint of Example IX was mixed with an equal weight of precipitated chalk to give a stiff paste which was molded into a marking crayon. After drying, marks were applied with this crayon to undyed fabrics of wool, cotton, viscose rayon, acetate rayon, nylon, Perlon, Type 42 Orlon, Acrilan, and Dacron. The marked fabrics were steamed for one hour at 160° F. dry bulb and 150° F. wet bulb temperatures, and also subjected to ironing at 160° F. When scoured at 120° F. for 5 minutes in a 0.1 percent solution of soap, the marks were completely removed from all samples.

Example XI

The ferrous chelate of 2,2'-bipyridine was prepared by dissolving one part of bipyridine in 100 parts of water and adding ferrous sulfate in 10 percent aqueous solution until color intensity reached a maximum. The bright red solution obtained was neutralized with sodium bicarbonate solution to pH 7 and filtered to remove the slight excess of iron.

Ten parts of poly-N-vinylcaprolactam, having a K value of 20, were dissolved in 100 parts of the above dye solution. Samples of Type 42 Orlon and viscose rayon staple were tinted by spraying with the resulting mixture. The tint was readily removable from these fibers by simple scouring of the type indicated in Example I.

Example XII

A red tinting solution was prepared from Neolan Red GRE, Prototype Number 391, a preformed chromium chelate of an O,O'-dihydroxy azo dye according to the formula listed below:

Component: Parts by weight

Neolan Red GRE 0.5
Poly-N-vinylpyrrolidone K-12 5.0
Water 94.5

This solution was applied by spraying to wool top, Type 42 Orlon staple, and viscose rayon staple. The steaming and scouring procedures were the same as in Example I, and the color was readily removed by scouring, leaving the fibers substantially white. Similar samples of these fibers, tinted with a solution which did not contain PVP, could not be scoured free of the dye.

Example XIII

A red tinting solution was prepared from Cibalan Scarlet GL, a neutral-dyeing chromium chelate of an O,O'-dihydroxy azo dye according to the formula listed below:

Component: Parts by weight

Cibalan Scarlet GL 0.5
Poly-N-vinylpyrrolidone K-30 5.0
Water 94.5

When the fibers listed in Example XII, steamed, and scoured, the color was found to be completely removed, leaving a white fiber substrate suitable for dyeing in pastel shades. This color applied to a solution containing no PVP, could not be scoured from the fibers after steaming.

While the examples set forth a variety of metals that may be used in effecting chelation, it will be obvious to the dye chemist that others could be employed to equally good advantage.

In some cases, Example IX for instance, chelation may take place in the presence of the poly-N-vinyl lactam. Ordinarily, however, it is preferred to form the chelate first, since as indicated by the examples a filtration step is frequently desirable and the higher viscosity of the lactam tends to hinder filtration.

Water solutions of poly-N-lactams support mold growth and it is generally desirable in cases, where the aqueous tint solutions are stored before use, to incorporate a mold inhibitor in the solution. Such compounds as salicylic acid, sodium benzoate and sodium pentachlorophenate are effective in concentrations between 0.01 and 0.05 percent based on the weight of solution. Sodium 2,4,5-trichlorophenate is even more effective and may be used in concentrations as low as 0.001 percent.

As will be observed from the examples, the tints of the present invention are preferably applied to the fibrous material in an aqueous solution. The amount of water employed may be widely varied dependent on the intensity desired in the tint and other considerations, all within the knowledge of the expert, but, of course, the amount must be sufficient to dissolve both the dyestuff and the polymer. Usually, fairly dilute solutions are most satisfactory and I have obtained good results using from 20 to 200 times as much water as dyestuff.

The manner in which the fibers are caused to be tinted may be any of those well known in the art. For example, the tint may be applied by spraying, brushing, padding, dipping or any other means. The particular stage of processing at which tinting takes place is a matter of individual preference. Thus, tinting may be practiced on the fibers when in relatively discrete form, as during opening and blending; or on strands or yarns, as during winding; or on wound packages of yarn, such as cones, pirns, bobbins and the like.

Having thus described my invention, what is claimed as new and desired to be secured by Letters Patent is:

1. As a fugitive tint for textile fibers, the product of the admixture in the presence of water of (1) a water soluble aromatic dyestuff having chromophoric and autochromic substituents and including a heterocyclic ring of from 5 to 6 members, one of said members being a metal atom united in the ring by a normal covalent bond on one side and a coordinate bond on the other, which dyestuff normally stains the textile fiber to be tinted, and (2) at least 50% by weight of said compound of a poly-N-vinyl lactam.

2. Textile fibers tinted with the product of claim 1.

3. A tint as in claim 1 wherein said product is in dilute aqueous solution and includes at least 10% by weight of said lactam of a plasticizer therefor.

4. A fugitive marking crayon for textile materials comprising a solid shaped mixture of the dry product of claim 1 and a substantial amount of a powered inert binder.

5. The product as in claim 1 wherein said lactam is poly-N-vinyl pyrrolidone.

6. Textile fibers tinted with the product of claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,072,870 Dreyfus Mar. 9, 1937
2,347,644 Self May 2, 1944
2,802,713 Opin et al. Aug. 13, 1957
2,802,714 Opin et al. Aug. 13, 1957

FOREIGN PATENTS

522,941 Belgium Oct. 15, 1953

OTHER REFERENCES

British Rayon and Silk Journal, April 19, 1953, p. 54.