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3,695,821

## PROCESS FOR FAST DYEING OF FIBRES AND SHAPED ARTICLES

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4 Claims

### ABSTRACT OF THE DISCLOSURE

Fibers or shaped articles made from fibers of hydrophobic polymeric hydrocarbon, chlorinated polymeric hydrocarbon or polyester which do not contain a polar group but which do contain a methyl, methylene or methine group or a benzene nucleus may be fast dyed by dyeing the fibers or shaped articles with a dyestuff containing a sulfon azide group by a conventional dyeing process, treating the dyed article to decompose the sulfon azide to sulfonyl nitrene which forms a covalent bond with the fiber and washing the fast dyed fiber to remove the excess dyestuff.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for fast dyeing of polymeric hydrocarbon, chlorinated polymeric hydrocarbon or polyester fibres or their shaped articles.

When dyeing polyester fibres, for example, they are usually dyed in a dispersion by high-pressure dyeing, carrier dyeing, or thermosol dyeing, but in these processes, fastness to sublimation is often unsatisfactory depending on the structure of the dyestuff.

However, fastness to sublimation and other fastness might be improved, if a dyestuff possessing a reactive group is used to react with fibres and to form a covalent bond, as conventional reactive dyestuffs are. The present inventors have noticed a methyl group (or a methylene group) or a benzene nucleus in a molecule of polyester or polypropylene fibres, and supposed that the fibres must be dyed with good fastness by a dyestuff having a reactive group reacting with said group or nucleus: after earnest researches, the present inventors have found that hydrophobic fibres without a reactive polar group can be dyed with good fastness by forming a dyestuff containing a sulfon azide group ( $-\text{SO}_2\text{N}_3$ ) on said fibres and then exposing those fibres to heat, steam or ultraviolet rays.

As the dyestuff which can be used according to the process of this invention, there are exemplified azo dyestuffs having a sulfon azide group in a molecule, anthraquinone dyestuffs, quinoline dyestuffs, methine dyestuffs, diphenylamine dyestuffs, indigoid dyestuffs, and nitro dyestuffs.

A process, in which a dyestuff containing a sulfon azide group is allowed to react with fibres having a so-called reactive group such as  $-\text{OH}$  group and  $-\text{NH}_2$  group, for example, cellulose fibres, acetate fibres and polyamide fibres, is found in Japanese patent publication No. 19233/1961. The so-called reactive groups of this patent are also polar groups. In the process of the present invention, however, dyed articles with good fastness is obtained by forming a covalent bond as allowing sulfonyl nitrene ( $-\text{SO}_2\text{N}$ ) produced by thermal decomposition or photolysis of a sulfon azide group to attack a methyl group (or a methylene or methine group) or a benzene nucleus in fibres possessing a reactive group but no polar group such as polyester fibres and polypropylene fibres, their shaped articles or polyethylene shaped articles. The reaction mechanism for the decomposition of sulfon azide and

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the attack of sulfonyl nitrene on a methyl group or a benzene nucleus is discussed by L. Horner and A. Christmann in *Angewandte Chemie*, 75. Jahrgang 1963, Nr. 15, pp. 707-16.

The process of this invention is substantially different from the process of Japanese patent publication No. 19233/1961 wherein a dyestuff reacts with a reactive polar group in a fibre from the standpoint of the reaction mechanism, and it is an absolutely novel process for dyeing.

The gist of the present invention is that polymeric hydrocarbon, chlorinated polymeric hydrocarbon or polyester fibres or their shaped articles (for example, film, sheet, etc.) are dyed with a dyestuff having a general formula,

$\text{D}-(\text{SO}_2\text{N}_3)_n$  (wherein  $\text{D}$ =chromogen,  $n$ =a positive integer) by a conventional dyeing process, such as high-pressure dyeing, carrier dyeing, and thermosol dyeing, and then they are exposed to heat, steam or ultraviolet rays at a temperature from 120 to 220° C. In thermosol dyeing, a good result is obtained by a usually employed process, and it is no need to repeat heat treatment and other treatment.

In said process, a sulfon azide group attacks a carbon atom in a methyl group (or a methylene or methine group) or a benzene nucleus to react via a sulfonylnitrene intermediate and a nitrogen-carbon bond is accomplished, as described previously.

The dyed articles thus obtained is further treated with an organic solvent and/or soaped to remove the unreacted dyestuff, and then water-washed and dried.

The dyed articles thus obtained have excellent fastness, and particularly, fastness to sublimation is so excellent as bleeding on the attached cloth (of polyester) is 4.5-5 class in the test performed at 200° C. for 1 minute.

As the fibres and shaped articles to be employed in the present invention, there are exemplified polyester, polypropylene, polyethylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, and chlorinated polyethylene.

The dyestuff having a sulfon azide group used in this invention is manufactured by the following method: a dyestuff is chlorosulfonated by a conventional method to introduce a sulfonyl chloride group, and the obtained chlorosulfonate is allowed to react with sodium azide to form a sulfon azide group.

It is also possible to allow hydrozine hydrate or hydrazine to react with said chlorosulfonate to form a sulfon hydrozide group with which sodium nitrite reacts to form a sulfon azide group.

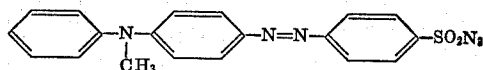
Alternatively, a dyestuff having a sulfonic acid group (or an intermediate containing a sulfonic acid group for forming such a dyestuff) is converted to sulfon halogenide by a usual method, and sulfon azide group is formed by the above-described method.

As to azo dyestuffs, when using an amino compound having a sulfon halogenide group as a diazo component, after forming a sulfon hydrozide group, a sulfon hydrozide group is converted to azide simultaneously to diazotization of an amine group by treating with nitrite and an acid.

The invention is explained more concretely as referring examples, in which parts are all by weight.

#### Example 1

In a dyebath prepared by adding to 4000 parts of water containing 1 part of sodium oleylsulfate a dispersion produced by grinding 1.5 part of a dyestuff represented by the following Formula I



(I)

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1.5 parts of a condensate of alkyl-naphthalene sulfonic acid as a dispersing agent and 0.7 part of sodium poly-alkyl-naphthalene sulfonate as a wetting agent together with water for a several hours, 100 parts of polyester fibre (for example, Tetron cloth) were immersed and dyed in a pressure container at 130° C. for 60 minutes. After water-washing the dyed fibre, it was treated at 160° C. for 30 minutes: it was immersed in N,N-dimethyl-formic amide at room temperature or an elevated temperature to remove completely the unreacted dyestuff, and then it was soaped, water-washed and dried to produce a fast dyed article, particularly an orange yellow dyed article having excellent fastness to sublimation.

Fastness to sublimation (200° C., 1 min.)

Alteration in colour: 4.5-5 class

Bleeding on Tetron: 4.5-5 class

Fastness to sublimation obtained by high-pressure dyeing without heat treatment was so poor as shown below.

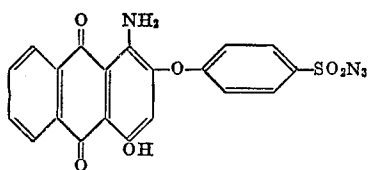
Fastness to sublimation (200° C., 1 min.)

Alteration in colour: 1 class (brown change)

Bleeding on Tetron: 1 class

#### Example 2

1.5 part of a dyestuff represented by the following general Formula II,



(II)

was dispersed and high-pressure dyeing, heat treatment and treatment with N,N-dimethylformic amide were performed, as similar in Example 1: thus, there was obtained a fast dyed article, particularly a clear bluish red polyester dyed article having excellent fastness to sublimation.

Fastness to sublimation (200° C., 1 min.)

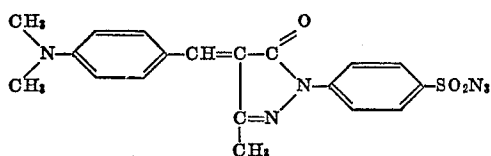
Alteration in colour: 5 class

Bleeding on Tetron: 4.5-5 class

The used dyestuff (II) was prepared as follows: 9.9 parts of 1-amino-2-phenoxy-4-hydroxy-anthraquinone synthesized by a publicly-known process were added to 75 parts of chlorosulfonic acid as cooling, and after the reaction at temperatures lower than 100° C., the reaction mixture was poured into ice to separate a crystal, which was filtered, and washed with iced water: then, the obtained chlorosulfonate was dissolved in 60 parts of formic amide, and allowed to react at 70-80° C. as adding a solution consisting of 3 parts of sodium azide and 30 parts of water: then, separated crystal was filtered, water-washed and dried.

#### Example 3

1.5 parts of a dyestuff represented by the following Formula III:



(III)

was dispersed by the same method as described in Example 1: in a dyebath consisting of said dispersion, 5 parts of a commercially available carrier (Carriant 323, manufactured by Toho Kagaku Co.) and 1500 parts of water, 100 parts of Tetron fabric was immersed. The dyebath was heated up to the boiling point within 30 minutes and the temperature was maintained for 60 minutes. The dyed article was water-washed, treated at 160° C. for

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30 minutes, and then immersed in N,N-dimethylformic amide: after extracting and removing the unreacted dyestuff at room temperature or an elevated temperature, it was soaped, water-washed and dried: thus, there was obtained a fast dyed article, particularly a clear yellow dyed article having excellent fastness to sublimation.

Fastness to sublimation (200° C., 1 min.)

Alteration in colour: 4.5-5 class

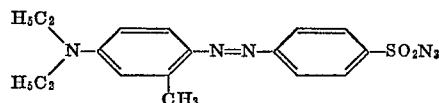
Bleeding on Tetron: 4.5-5 class

The used methine dyestuff (III) was prepared as follows: 16 parts of 1-(benzene-4-sodium sulfonate)-3-methyl-5-pyrazolone and 9 parts of 4-N,N-dimethyl-aminobenzaldehyde were allowed to react with each other in the presence of a catalytic amount of glacial acetic acid in 200 parts of methanol for 2 hours at the boiling point; after cooling, the separated crystal was filtered and dried sufficiently. 16 parts of the dyestuff was suspended in 160 parts of chlorobenzene, and after adding 3.2 parts of N,N-dimethylformic amide and 7.2 parts of thionylchloride, reaction was carried out at 80° C. for 1 hour; after cooling with ice, the obtained crystal was filtered and allowed to react with sodium amide by the same method for manufacturing the dyestuff (II) used in Example 1.

The dyestuff (III) may be prepared by the reaction with hydrazine hydrate at 25° C. after converting to chlorosulfonate, and after converting to sulfonic hydrazide, adding an aqueous solution of sodium nitrite to convert to azide.

#### Example 4

1.5 part of a dyestuff represented by the following general Formula IV:



(IV)

was dispersed by the same process as described in Example 1, and a dyebath was prepared together with 2000 parts of water. 100 parts of polypropylene fibres refined by a conventional process were immersed in it, and kept there at 100° C. for 90 minutes. After water-washing, the fibres were treated at 130-140° C. for 2 hours, followed by extracting the unreacted dyestuff by heating in N,N-dimethyl formic amide. There was obtained a yellowish fast dyed article after water-washing and drying.

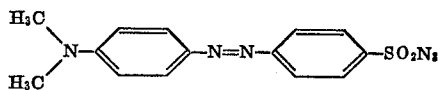
Fastness to dry cleaning (JIS L 1006): 5 class

Quite the same process can be applied to dyeing of polypropylene film instead of polypropylene fibres, and a good result can be obtained.

The used azo dyestuff (IV) was prepared as follows: 14 parts of 4-amino-phenyl-sulfonic hydrazide were dissolved in a solution consisting of 45 parts of concentrated hydrochloric acid and 200 parts of water, and as cooling at temperatures lower than 5° C., a solution consisting of 11 parts of sodium nitrite and 100 parts of water was dripped: reaction was performed for 1 hour at temperatures lower than 10° C. to form diazo and diazide and then added gradually to a solution consisting of 12 parts of N,N-diethyl-m-toluidine and 200 parts of methanol as cooling. Coupling was performed at 10-15° C. and the separated crystal was filtered and dried in vacuum.

#### Example 5

1.5 parts of a dyestuff represented by the following general Formula V:



(V)

was treated similarly as described in Example 1 to prepare a dyebath, in which 100 parts of polyester film were

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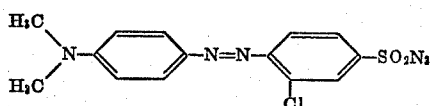
immersed and dyed in a pressure container at 120° C. for 60 minutes.

After heating the dyed film at 160° C. for 20 minutes, the unreacted dyestuff as extracted with N,N-dimethylformic amide at room temperature or an elevated temperature, and after water-washing, it was dried. Thus, polyester film can be fast dyed to yellow.

The used dyestuff (V) was prepared as similar to the dyestuff (IV), except that N,N-dimethyl-aniline was used instead of N,N-diethyl-m-toluidine.

#### Example 6

1.5 parts of a dyestuff (VI) represented by the following general Formula VI:



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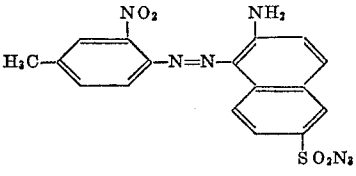
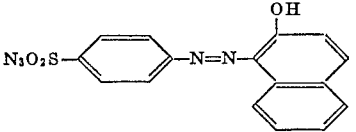
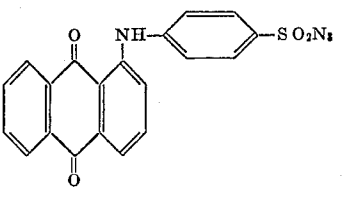
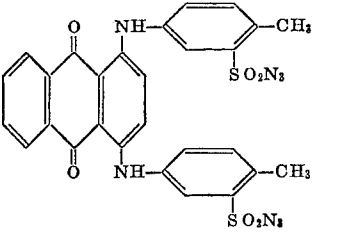
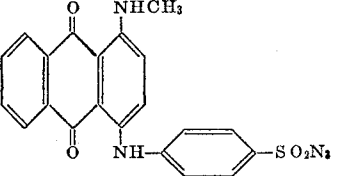
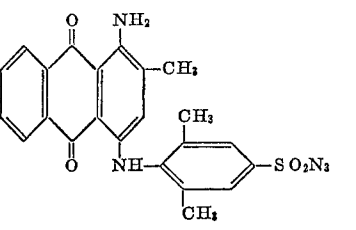
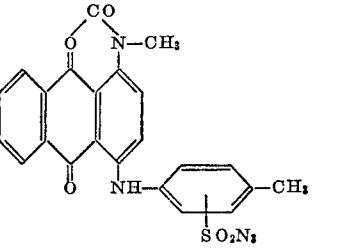
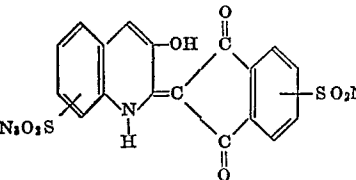
was treated similarly as described in Example 1 to prepare a dyebath, in which 100 parts of polypropylene film were immersed: after keeping them in the dyebath at 100° C. for 90 minutes, they were water-washed. Then, the dye film was exposed to ultraviolet rays by means of a high-pressure mercury lamp for 15 minutes at room temperature. The unreacted dyestuff was extracted in trichloroethylene at room temperature, and the film was water-washed to obtain yellow dyed polypropylene film.

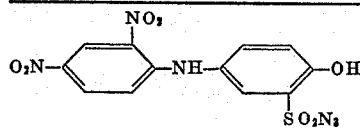
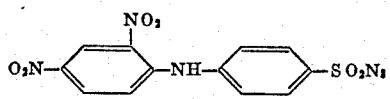
The used dyestuff (V) was prepared similarly to the dyestuff (IV), except that 4-amino-3-chlorophenyl-sulfonic hydrazide was used instead of 4-aminophenyl-sulfonic hydrazide and N,N-dimethylaniline instead of N,N-diethyl-m-toluidine.

#### Example 7

Using each 1.5 part of the dyestuffs shown by the following Formulae VII-XXVII, polyester fibres were dyed by the same method as described in Example 1, and there could be obtained fast dyed articles having the hue shown in the right side, particularly dyed articles having excellent fastness to sublimation.

Dyestuff		Hue of polyester fibre
	(VII)	Yellow.
	(VIII)	Orange.
	(IX)	Do.
	(X)	Orange-yellow.
	(XI)	Orange.
	(XII)	Do.
	(XIII)	Yellowish-brown.
	(XIV)	Orange-yellow.
	(XV)	Yellow.
	(XVI)	Yellowish-orange.
	(XVII)	Red.

Dyestuff	Hue of polyester fibre
	(XVIII) Red.
	(XIX) Reddish-brown.
	(XX) Reddish-violet.
	(XXI) Greenish-blue.
	(XXII) Blue.
	(XXIII) Do.
	(XXIV) Red.
	(XXV) Yellow.

Dyestuff	Hue of polyester fibre
	(XXVI) Yellowish-orange.
	(XXVII) Yellow.

We claim:

1. A process for fast dyeing polymeric hydrocarbon, chlorinated polymeric hydrocarbon or polyester fibers which do not contain a polar group but which do contain at least one of the following: a methyl, methylene, or methine group or a benzene nucleus, or a shaped article made from such fibers comprising: dyeing the fibers or shaped articles with a dyestuff containing a sulfon azide group; exposing the dyestuff molecules attached to the fibers or shaped article to heat, steam or ultra-violet rays to a degree and for a length of time sufficient to decompose the sulfon azide to sulfonyl nitrene, which then forms a covalent bond to the methyl, methylene or methine group, or the benzene nucleus of the fibers or shaped article.

2. The fast dyeing process of claim 1, wherein the sulfon azide groups of the dyestuff molecules attached to the fibers or shaped article are decomposed by heating the fibers or shaped article after the completion of the dyeing process at a temperature from 120-220° C.

3. The fast dyeing process of claim 1, wherein the sulfon azide groups of the dyestuff molecules attached to

the fibers or shaped article are decomposed during the dyeing step by use of thermosol dyeing.

4. The fast dyeing process of claim 1, wherein the sulfon azide groups of the dyestuff molecules attached to the fibers or shaped article are decomposed by exposing the fibers or shaped article after completion of the dyeing process to ultraviolet radiation.

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Homer et al., Angewandte Chemie, 75, January 1963, pp. 707-16.

GEORGE F. LESMES, Primary Examiner

J. T. BRAMMER, Assistant Examiner

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8-4, 163; 204-158