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PROCESS FOR IMPROVING THE AFFINITY FOR DYES OF SHAPED POLYOLEFINE ARTICLES

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This invention relates to a process for improving the affinity for dyes of shaped articles consisting of polyolefines, and more particularly to the treatment of textile articles formed of polyolefines.

Shaped articles consisting of polyolefines cannot be dyed satisfactorily by direct application of dyes by the normal techniques employed in the dyeing art.

It has been proposed, in an effort to increase the affinity of the polyolefines for dyes, to modify the surface of the polyolefines either by chemical action or by irradiation followed by grafting of monomeric compounds.

This chemical modification can be effected by the successive treatments:

(1) The action of oxidising agents such as halogens under certain conditions, or of true oxidising agents, such as ozone or mixtures of sulphuric acid and an alkali metal bichromate at room temperature;

(2) The action on the surface thus modified of a chemical compound reacting with the acid or ketone groups formed by the action of the oxidising agent.

The oxidation processes which constitute the first phase produce in themselves, under the described conditions, only a small improvement in the affinity of the polyolefine for dyes, and the application of the subsequent grafting processes is relatively complex and therefore costly.

It is an object of the present invention to provide a new process of considerable efficiency for treating polyolefine articles to enhance their affinity for dyes.

According to the present invention there is provided a process for the treatment of shaped articles containing or consisting of polyolefines to increase their affinity for dyes, which comprises treating the said articles first in an acid bath containing an alkali metal bichromate and the in an acid bath containing a reducing agent, the temperature of each bath being at least 80° C.

When the articles consist of polyethylene, the temperature of the bath containing the bichromate should preferably not exceed 105° C. When the articles consist of polypropylene, this temperature should preferably not exceed 120° C.

In the course of the foregoing treatment, the hexavalent chromium is reduced to trivalent chromium, which is then fixed in the material. Polyolefine articles containing more than 0.01% of chemically fixed chromium possess good affinity for plastosoluble dyes, basic dyes and metalliferous acid dyes. The treatment is without important effect on the physical properties of the articles treated.

The process of the invention makes it possible to improve the affinity for dyes of all textile articles consisting of polyolefines, such as filaments, fibres, continuous filament and staple fibre yarns, tows, mono-filaments, cables or woven fabrics, as also of other shaped articles, as well as for non-textile articles such as films, sheets and profiled articles generally.

The first treatment bath preferably contains at least 25 g./litre of the alkali metal bichromate. It may be made acid by means of any strong acid, sulphuric acid or hydrochloric acid being preferred.

By adding to the first bath a wetting agent which is normally stable in acid medium, such for example as the products of condensation of ethylene oxide with long-

chain sulphonated fatty alcohols, the chemical fixation of the chromium on the polyolefines is greatly facilitated.

The duration of the first treatment may vary e.g. from 5 to 30 minutes, and may even be prolonged for several hours without damage to the article to be treated.

The second acid treatment bath preferably contains up to 50 g./litre of a sulphite or of another strong reducing agent, such as sodium formaldehyde sulphoxylate. Higher concentrations may be employed if desired.

The following examples will serve to illustrate the invention:

Example I

Various samples of polyethylene yarn of high density (0.95) are treated at 100° C. for varying times in a bath containing, per litre:

200 cc. of sulphuric acid (66° Bé.),
50 g. of potassium bichromate, and
1 g. of the condensation product of ethylene oxide with a long-chained fatty alcohol.

The filaments are thereafter treated for one hour in a second bath at 80° C. containing

5 cc. per litre of a sodium bisulphite solution (36° Bé.), and
5 cc. per litre of sulphuric acid (66° Bé.).

After washing and drying, the various yarn specimens contain the following quantities of fixed trivalent chromium.

Duration of the oxidising treatment:	Percent Cr ··· on yarn
5 minutes	0.061
15 minutes	0.111
30 minutes	0.157
60 minutes	0.220
120 minutes	0.285

These specimens have then acquired very good affinity for plasti-soluble dyes, basic dyes and acid metalliferous dyes, their dyeing affinity being higher as the chromium content is higher.

All these specimens have substantially the same strength as before the treatment.

Example II

A jersey manufactured of high-density (0.96) polyethylene yarns is treated for half an hour in a first bath as in Example I.

After washing and reducing treatment in a second bath, as in Example I, the chromium content is 0.157%.

This jersey dyes very well with Ecarlate Orasol 2B (Colour Index, p. 2845) which imparts a fine red coloration thereto. No degradation of the mechanical properties of the fibre was observed.

Example III

A woven fabric formed of continuous polypropylene yarns is treated for one hour at 100° C. in a bath containing, per litre:

250 cc. of sulphuric acid (66° Bé.),
55 g. of sodium bichromate,
1.5 g. of the condensation product of ethylene oxide and long chain fatty alcohol, used in Example I.

After rinsing, the fabric is treated for 1½ hours at 95° C. in a bath containing, per litre:

6 cc. of sodium bisulphite solution (36° Bé.),
1 cc. of hydrochloric acid (22° Bé.).

After washing and drying the fabric the fixed trivalent chromium content was found to be 0.05%.

This fabric dyes very well with 4.5% of the dye Bleu

Celanthrene FFSK (Colour Index No. 61505), the hue being very bright and intense.

Example IV

Polypropylene fibre is treated for 2 hours at 100° C. in an oxidising bath containing acid potassium bichromate.

After treatment in the reducing bath as in Example III, the fixed trivalent chromium content was found to be 0.100%.

This fibre dyes very well at 98° C. with the dye Orange Astrazon R (Colour Index No. 48040).

The hue is very vivid and pleasant.

Example V

A woven fabric consisting of polyethylene yarns (the polyethylene having been produced by high pressure polymerisation) is treated at 105° C. in a pressure-resistant stainless steel apparatus for 5 minutes, in a bath containing, per litre:

100 cc. of sulphuric acid (66° Bé.),
25 g. of sodium bichromate.

The fabric is wrung out and treated for one hour in a second bath at 98° C. containing 20 g./litre of sodium formaldehyde sulphoxylate.

After washing, the fabric is dyed without difficulty in one hour at 98° C. with the basic dye Orange Astrazon R (Colour Index No. 48040).

The fabric is dyed with a fine, very bright orange hue.

I claim:

1. A process for the treatment of shaped aliphatic polyolefine articles to increase their affinity for dyes which comprises contacting the said shaped articles first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with an acid bath containing a reducing agent, the temperature of each bath being at least 80° C.

2. A process for the treatment of filamentary aliphatic polyolefine material to increase its affinity for dyes which comprises contacting the said filamentary material first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with an acid bath containing a reducing agent, the temperature of each bath being at least 80° C.

3. A process for the treatment of filamentary aliphatic polyolefine material to increase its affinity for dyes which comprises contacting the said filamentary material first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with an acid bath containing a sulphite reducing agent, the temperature of each bath being at least 80° C.

4. A process for the treatment of filamentary aliphatic polyolefine material to increase its affinity for dyes which comprises contacting the said filamentary material first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with an acid bath containing sodium formaldehyde sulphoxylate, the temperature of each bath being at least 80° C.

5. A process for the treatment of filamentary aliphatic polyolefine material to increase its affinity for dyes which comprises contacting the said filamentary material first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with an acid bath containing a reducing agent, the temperature of each bath being 80 to 120° C.

6. A process of the treatment of filamentary aliphatic polyolefine material to increase its affinity for dyes which comprises contacting the said filamentary material first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with a hydrochloric acid bath containing up to 50 g./litre of a sulphite, the temperature of each bath being at least 80° C.

7. A process for the treatment of filamentary aliphatic polyolefine material to increase its affinity for dyes which comprises contacting the said filamentary material first with a bath containing, per litre, 25 to 55 grams of alkali metal bichromate and 100–250 cc. of concentrated sulphuric acid, for 5 to 120 minutes, and then with a hydrochloric acid bath containing up to 50 g./litre of sodium formaldehyde sulphoxylate, the temperature of each bath being at least 80° C.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 24,062	Horton	Sept. 20, 1955
1,957,491	Dreyfus et al.	May 8, 1934
2,400,720	Staudinger et al.	May 21, 1954
2,668,134	Horton	Feb. 2, 1954
2,865,880	Caldwell	Dec. 23, 1958
2,886,471	Bruce et al.	May 12, 1959

OTHER REFERENCES

Widmar et al.: O.G., March 24, 1951, vol. 644, p. 914.