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PRINTING ANIMAL FIBERS

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The present invention relates to compositions of matter useful for printing animal fibers, particularly such as contain a vat-dyestuff and amine-bases of the aliphatic series and to a process of printing vat-dyestuffs on animal fibers and textiles containing animal fibers.

In the printing of vat-dyestuffs on animal fibers, especially on wool, various processes are known for preventing deleterious effects of the alkali, for instance of the most frequently used alkali carbonate. In German Patent No. 391,995 there are, used, for instance, ammonia, ammonium carbonate or ammonium bicarbonate or mixtures thereof instead of alkali carbonate or alkali hydroxide. Most of the vat-dyestuffs, however, when printed according to this method of working, as well as other methods using alkali salts of acids which are more feeble than carbonic acid, such as phosphates, phenolates and the like, yield prints of less intensity; only some vat-dyestuffs which may easily be reduced, such as thioindigo, may be applied. In another process, described in U. S. Patent No. 1,990,852, amino-acetic acid is added as protective agent for the fiber to the printing colors which, as usual, contain an alkali carbonate; the process permits the use of the wool-dyeing vat-dyestuffs in printing, for the most part with good result, but it has been found that, in spite of this protective agent for the fiber, detrimental effects of the alkali carbonate are not always excluded so that sometimes the feel, the weave or interlacing of the fabric and the elasticity of the fiber are not sufficiently protected and preserved; thus the weave may be impaired by shrinkage or felting of the threads.

I have found that the deleterious influence of the usual alkalis on woolen fibers is minimized or entirely avoided by wholly or substantially replacing the aforesaid alkalis either by amine-bases of the aliphatic series which contain at least two basic nitrogen atoms. Such amine-bases are, for instance, ethylenediamine, polyethylenediamines, hydroxy-ethyl-polyethylenediamines, triethylenetetramine, hydroxy-ethyl-hexamethylenetetramine. There may also be used the products of the co-pending U. S. Patent application Serial No. 31,734, filed July 16, 1935, in the name of Max Paquin, for "Condensation products and a process of preparing them", obtainable by condensing urea or the derivatives thereof with such hydroxy-alkylamines as are obtainable by the action of an alkyleneoxide on an organic compound having at least two amino-groups. As in the above-mentioned process of U. S. Patent No. 1,990,852 there may be obtained very brilliant and intense prints with vat-dyestuffs on animal fibers when working according to the process of this invention. Moreover, these

prints surpass those obtained by known processes, for instance, as to the strength and evenness of the prints, the feel, the elasticity and the weave of the fabric. The natural softness of the fiber is by no means impaired and shrinking of the threads is practically avoided.

The invention is applicable to wool and mixtures of wool with other animal or vegetable fibers (for instance, half-wool or wool mixed with artificial fibers such as spun rayon, acetate artificial silk and the like) as well as to silk and mixtures thereof and to vegetable natural and artificial fibers. The printing colors may be used in direct printing processes as well as in the form of a discharge paste on pre-dyed material; furthermore for padding for which purpose less thickening agent is added in order to obtain a lower viscosity. They may be used either in an unreduced or reduced state. There may also be added to the printing color, besides glycerine, the usual auxiliary agents such as sodium benzylsulfanilate, thiodiglycol, glycols, urea, glucose and the like. The latter may substitute either partly or, if desired, wholly the sodium formaldehyde sulfoxylate used in printing pastes.

It is also possible to make vat-dyestuff preparations which are ready for use with addition of the aforesaid compounds; they may then be used for incorporation in printing preparations.

The above-mentioned amine-bases of the aliphatic series having at least 2 nitrogen atoms are obtainable in the following manner:

Polyethylenediamines are amines of the general formula: $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2$, wherein n represents an unknown higher number. These substances are formed as by-products in the preparation of ethylenediamine, described in Beilstein "Handbuch der organischen Chemie", 4th edit., vol. 4, page 230. The known process yields a product from which there is obtainable at first ethylene-diamine by fractional distillation and then at a higher temperature, for instance, at about 220° C. to about 290° C., the polyethylenediamines.

Hydroxy-ethyl-polyethylenediamines are obtainable by introduction of gaseous ethylene oxide into polyethylenediamines heated to 100° C., whereby one hydrogen atom of the terminal NH_2 -group is exchanged by the $-\text{CH}_2\text{CH}_2\text{OH}$ -group.

Hydroxyethyl hexamethylenetetramine is obtainable by introduction of ethyleneoxide into molten hexamethylenetetramine.

Triethylenetetramine is described in the literature, cf., for instance, Beilstein, "Handbuch der organischen Chemie", 4th edit., vol. 4, page 255, below.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto.

1. A printing paste is prepared from:

	Grams
Dyestuff No. 1356 (Schultz, Farbstoffta- bellen, 7th edit., vol. I) -----	200
5 Glycerine -----	80
Water -----	50
Thickening -----	450
Ethylenediamine -----	150
10 Sodium formaldehyde sulfoxylate -----	70
	1,000

After printing and drying, the material is steamed in a Mother-Platt apparatus free from air, reoxidized in known manner, rinsed and if desired after-treated with a solution containing a wetting agent.

2. A printing paste is prepared from:

	Grams
20 Dyestuff No. 1349 (Schultz, Farbstoffta- bellen, 7th edit., Vol I) -----	200
Glycerine -----	80
Water -----	40
Thickening -----	400
25 Hydroxyethyl-polyethylenediamine -----	150
Glucose -----	100
Sodium formaldehyde sulfoxylate -----	30
	1,000

30 The fibers which have been treated with this printing color are after-treated as described in Example 1.

3. A printing paste is prepared from:

	Grams
35 Dyestuff No. 1269 (Schultz, Farbstoffta- bellen, 7th edit. Vol. I) -----	100
Glycerine -----	80
Water -----	100
40 Thickening -----	450
Triethylenetetramine or hydroxyethylhexa- methylenetetramine -----	200
Sodium formaldehyde sulfoxylate -----	70
	1,000

45 The fibers are after-treated as described in Example 1.

4. A printing paste is prepared from:

	Grams
50 Dyestuff No. 1314 (Schultz, Farbstoffta- bellen, 7th edit., Vol. I) -----	150
Glycerine -----	80
Water -----	100
55 Thickening -----	450
Condensation product of hydroxyethylpoly- ethylenediamine with urea -----	150
Sodium formaldehyde sulfoxylate -----	70
	1,000

The fibers are after-treated as described in Example 1.

In the preceding examples there may be used as thickening, for instance, British gum or gum thickening.

I claim:

1. In the process of printing a vat-dyestuff printing on animal fibers and textiles contain-
ing animal fibers the step which consists in using as alkaline substance necessary for the printing process an amino-compound of the group consisting of ethylenediamine, polyethylenediamines, hydroxy-ethyl-polyethylelediamines, triethylenetetramine, hydroxy-ethyl-hexamethylenetetramine and the urea-condensation products of hydroxyalkylamino-compounds obtained by the action of an alkyleneoxide on an organic compound containing at least two amino-groups.

2. In the process of printing a vat-dyestuff printing on animal fibers and textiles contain-
ing animal fibers the step which consists in using as alkaline substance necessary for the printing process ethylenediamine.

3. In the process of printing a vat-dyestuff printing on animal fibers and textiles contain-
ing animal fibers the step which consists in using as alkaline substance necessary for the printing process hydroxy-ethyl-polyethylenediamine.

4. In the process of printing a vat-dyesuff printing on animal fibers and textiles contain-
ing animal fibers the step which consists in using as alkaline substance necessary for the printing process triethylenetetramine.

5. Compositions of matter containing a vat-dyestuff, a thickening agent, a reducing agent and, as alkaline substance necessary for the printing process, an amino-compound of the group consisting of ethylenediamine, polyethylenediamines, hydroxy-ethyl-polyethylenediamines, triethylenetetramine, hydroxy-ethyl-hexamethylenetetramine and the urea-condensation products of hydroxyalkylamino-compounds obtained by the action of an alkyleneoxide on an organic compound containing at least two amino-groups.

6. Compositions of matter containing a vat-dyestuff, a thickening agent, a reducing agent and, as alkaline substance necessary for the printing process, ethylenediamine.

7. Compositions of matter containing a vat-dyestuff, a thickening agent, a reducing agent and, as alkaline substance necessary for the printing process, hydroxy-ethylpolyethylenediamine.

8. Compositions of matter containing a vat-dyestuff, a thickening agent, a reducing agent and, as alkaline substance necessary for the printing process, triethylenetetramine.

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