

2.474.908

Henry Charles Olpin, Philip Broughton Law, and Sydney Alfred Gibson, Spondon, near Derby, England, assignors, by meane assignments, to Celanese Corporation of America, a corporation of Delaware

**No Drawing. Application May 8, 1945,
Serial No. 592,726**

2 Claims. (Cl. 117—161)

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The ornamenting of textile fabrics by fixation of white or coloured pigments thereon has long been practised. Very attractive effects can be obtained by printing a lustrous textile fabric, for example one made from yarns of artificial continuous filaments, with a white pigment, for example titanium dioxide, in conjunction with an adhesive. It is highly desirable that the adhesive employed should effectively fix the pigment so that it resists removal by washing and does not dust off and further that the adhesive should be colourless and should not materially affect the handle of the textile materials. Moreover the adhesive and any treatment necessary to render it effective, for example steaming or heating, should not be such as to damage the fabric. Albumen has commonly been employed as an adhesive for the foregoing purpose, the material being printed with a preparation comprising the pigment and a suitable albumen (usually egg albumen) and then steamed to render the albumen employed insoluble in water. The albumens suitable for use in this process are somewhat variable in quality and price and tend to stiffen the fabrics unduly. Various synthetic resins derived from formaldehyde have been tried in place of albumen, the resin being applied to the fabric in water-soluble form and then converted into an insoluble form by heating. However many such resins develop colour during the heating and others require for their insolubilisation temperatures so high as to involve risk of damaging textile materials. Temperatures much above 100° C. are further not conveniently attainable in the machines commonly available in textile printing works.

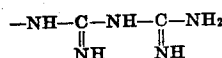
We have now found that the condensation products of formaldehyde or other aliphatic aldehyde with substitution products of biguanide are particularly effective for fixing pigments on textile material. Thus a thickened preparation containing titanium dioxide, and a water-soluble condensation product of formaldehyde and ethylene di-biguanide can be printed on a lustrous fabric of artificial filaments and then heated to insolubilise the condensation product. The titanium dioxide is well fixed and forms a dull pattern on a lustrous ground. Fixation can be effected at a low temperature, for example as low as 90° C. and the material has a soft handle.

The substitution products of biguanides can be alkyl, aralkyl, cyclo-alkyl, or aryl substitution products, and include compounds in which more

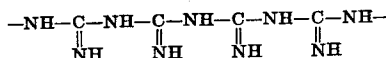
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than one biguanide radicle is attached to a single organic residue as in alkylene-di-biguanides. Such substituted biguanides can be obtained by the action of dicyandiamide on the hydrochloride of the appropriate alkyl-, aralkyl-, cyclo-alkyl- or aryl-amine. Primary or secondary amines can be used. Thus mono-biguanides can be obtained from dicyandiamide and ethylamine, di-ethylamine, hydroxyethylamine, propylamine, butylamine, 2-hydroxy-propylamine, benzylamine, aniline, toluidines, and methoxy-anilines, and di-biguanides from ethylene-diamine, alpha-beta-diamino-propane, trimethylene diamine, and hexamethylene diamine and other alkylene diamines.

The reaction between dicyandiamide and an amine hydrochloride is conveniently effected by heating at temperatures of the order of 150–200° C. It appears that the reaction often proceeds, at least in part, beyond the formation of the simple biguanide radicle



25 since some ammonia is given off. Possibly two biguanide radicles lose ammonia with formation of a polyguanide radicle such as



The biguanide derivatives obtainable by heating hydrochlorides of amines with dicyandiamide are well suited for use according to the invention.

For the purposes of the present invention the biguanide derivatives are best converted into water-soluble condensation products by reaction with formaldehyde, acetaldehyde or other aliphatic aldehyde. Formaldehyde is the preferred aldehyde and may be used in the form of 25 to 40 per cent aqueous solutions to react with the biguanide derivative; further additions are usually not essential.

The water-soluble condensation product is then applied to the textile material in conjunction with the pigment to be fixed. The preparation applied to the fabric may be thickened with one of the thickeners usually employed in the preparation of textile printing pastes, for example gum tragacanth. Further it may contain an acid or other substance capable for promoting the conversion of the water-soluble condensation product to a water-insoluble product on heating. Solid hydroxy aliphatic acids such as tartaric acid, citric acid, lactic acid, and other difficultly volatile or non-volatile organic acids are suitable for this

purpose. Again, weak inorganic acids such as boric acid may be used.

The application of the compositions containing the water-soluble condensation product and pigment to textile materials can be effected in various ways, the choice depending on the effects required. Thus they can be applied locally by printing or stencilling methods in any desired patterns. Again they may be applied to the whole surface of the fabric, e. g. by "all over" printing with an engraved roll.

Conversion of the water-soluble condensation product to water-insoluble form on the material can be effected by heating the material. Temperatures of 80° C. to 130° C. can be used though a temperature of about 90° C. is often sufficient. The heating can be effected by passing the textile material through an oven at the requisite temperature. Again it can be effected on an ordinary stentering machine, the temperatures of 80° C. to 100° C. readily attainable with these machines usually sufficient to insolubilise the condensation product. The duration of the heating may be 2 to 10 minutes.

After the heating the material is preferably rinsed and soaped to remove thickening agent and other unwanted matter.

The process is particularly useful for fixing white pigments on textile materials, for example titanium dioxide or barium sulphate. Coloured pigments may be similarly fixed, for example inorganic pigments, e. g. Prussian blue, ultramarine, lead chromate, cadmium chromate, or iron oxide, or organic pigments, e. g. phthalocyanine dyes, vat dyes and water-insoluble azo dyes having little or no direct affinity for textile materials.

Various textile materials whether of natural or artificial fibres may have pigments fixed on them by the new process. The textile material may be of fibres of natural silk, natural or regenerated cellulose, or cellulose acetate or other cellulose ester or ether. Fixation of white pigments is of greatest value on lustrous textile fabrics of artificial fibres, by reason of the attractive effects which can be obtained. Such artificial fibres may be continuous filaments of regenerated cellulose spun by the viscose or cuprammonium process or obtained by saponification of cellulose ester fibres which have been stretched, e. g. in steam or hot water. Again the treatment may be applied to lustrous textile fabrics of continuous filaments of cellulose acetate or other cellulose ester or ether, e. g. cellulose propionate, butyrate, acetopropionate, or acetobutyrate, or of ethyl cellulose or other ether of cellulose.

The invention is illustrated by the following example in which the "parts" referred to are parts by weight:

Example

4 parts of ethylene diamine hydrochloride and 5 parts of dicyandiamide are melted together at 120° C. to 140° C. and the temperature slowly raised to 200° C. which is maintained for 7 hours during which time ammonia is evolved. 18 parts of the product are warmed to 70° C. for 1 hour with 33 parts of aqueous formaldehyde of 40 per

cent strength; after cooling, 2.7 parts of tartaric acid are then added. The resulting solution is stable, no precipitate forming on standing for several days. The following printing paste is then prepared:

	Parts
Gum tragacanth (6%) (not neutralised)	50
The above solution	8
Titanium dioxide (50% aqueous paste)	15
Water	27

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A lustrous cellulose acetate satin fabric is printed with this paste and then passed through a stenter at a temperature of 90° C., the time of passage being 3 minutes. The material is then rinsed in cold water for 30 minutes, soaped in a 0.5 gram per litre soap solution for 10 minutes at 40° C., and finally again rinsed.

A pure white dull pattern on a lustrous ground is obtained which is exceedingly resistant to washing. Moreover the outlines of the pattern are sharp and the fabric has a soft handle and is free from the undesirable "boardiness" and cockling often associated with albumen prints.

By replacing the ethylene diamine hydrochloride by an equivalent amount of hexamethylene diamine hydrochloride similar results can be obtained.

Having described our invention, what we desire to secure by Letters Patent is:

1. A process for fixing pigments on artificial textile material, which comprises applying to the material an aqueous paste, comprising the pigment, an organic acid of low volatility and a water-soluble condensation product of formaldehyde and a substitution product of biguanide obtainable by heating dicyandiamide with ethylene diamine dihydrochloride to 150°-200° C., and then heating the material to a temperature of 80°-100° C.

2. Textile materials made up of continuous artificial filament yarns and having a pigment fixed thereon by means of a water-insoluble condensation product of formaldehyde and a substitution product of biguanide obtainable by heating dicyandiamide with ethylene diamine dihydrochloride to 150°-200° C.

HENRY CHARLES OLPIN.
PHILIP BROUGHTON LAW.
SYDNEY ALFRED GIBSON.

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