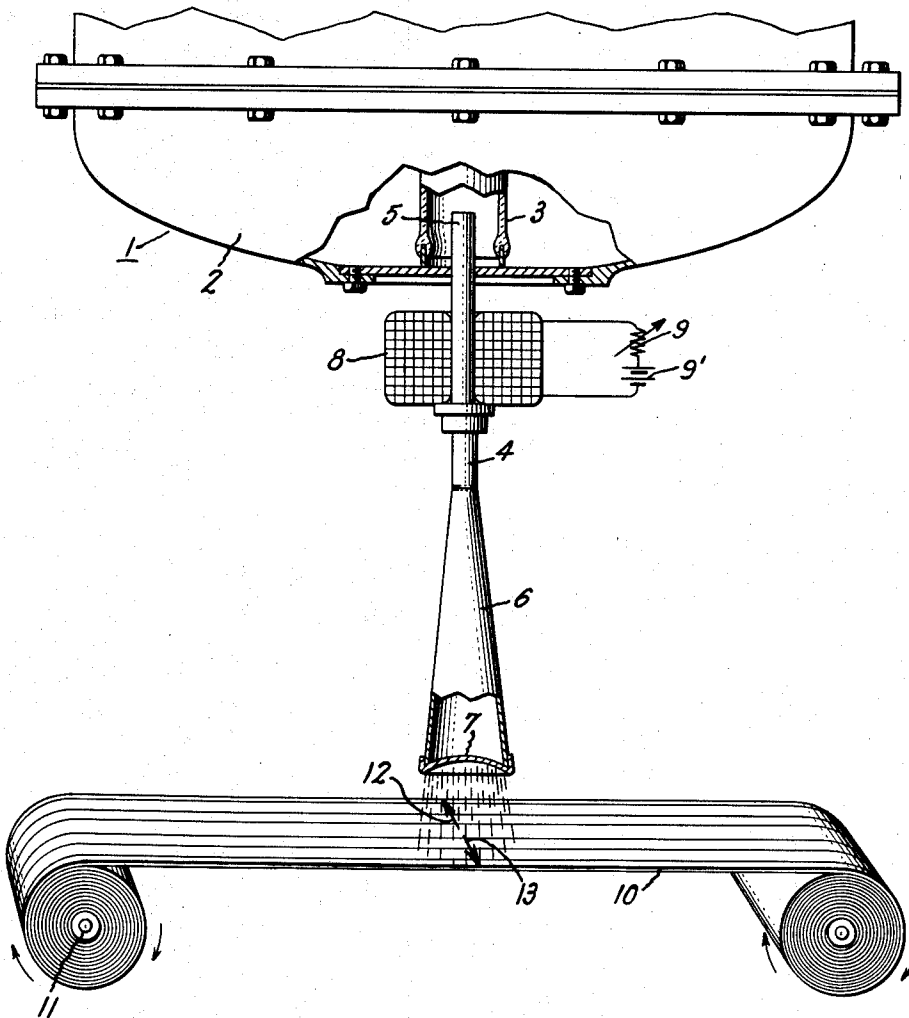


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PROCESS FOR IMPROVING THE CROCKING AND
COLOR-FASTNESS OF PIGMENT-PRINTED
FIBROUS SHEETS BY IRRADIATION
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1

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PROCESS FOR IMPROVING THE CROCKING AND COLOR-FASTNESS OF PIGMENT-PRINTED FIBROUS SHEETS BY IRRADIATION

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This application is a continuation-in-part of our co-pending application, Serial No. 324,553, now abandoned, filed December 6, 1952, and assigned to the same assignee as the present invention.

The present invention is concerned with improving the properties of fibrous sheet material or substrate printed with various pigments. More particularly, the invention relates to improving the properties of fibrous sheet materials such as, paper, textile materials, etc., containing printing thereon comprising a pigment bonded to the said sheet material by a resinous binder convertible by irradiation with high energy electrons to higher molecular weight compositions, which comprises irradiating the aforesaid pigment-printed fibrous sheet material with high energy electrons.

The term "textile materials" as employed herein and in the appended claims is intended to include such textiles (either in sheet, tape, etc., form) as, for example, cloth or fabric made of cotton, wool, silk, rayon, nylon, polyacrylonitrile, polyester fibers, etc.

In the printing of various textile materials, the type of printing deposited on such textiles may be classified as either dyestuff printing or pigment printing. In both these types of printing, essentially the same type of machinery is employed, namely, the printing is carried out on a rotary intaglio printing machine. The main differences between the two methods of printing lie in the method of coloring or printing the textile.

In carrying out the printing of textiles using dyestuffs, the latter are usually suspended in a highly viscous starch-water printing medium which is applied and printed onto the cloth by the printing machine according to the designs cut in the intaglio rollers of the printing machines. One disadvantage of employing dyestuff for printing purposes on the textiles, is the fact that as the dyestuff prints leave the printing machine, the ultimate final color and style of the finished printing are not completely apparent or visible to the operator of the printing machine; this is due to the fact that after the dyestuff ingredient has been applied to the textile, it is necessary to cause the color in the dyestuff to develop and affix itself to the fibers of the textile material. This is usually done by passing the printed cloth through an acid developing box called an "acid-ager." This causes the dyestuff ingredients to undergo reaction and to form the desired color or colors. After this reaction has been accomplished, it is then necessary to remove the unreacted ingredients and by-products from the cloth by a cumbersome process of washing. After this, since the dyestuff is developed within the fibers of the textile material, it is "substantive" to the fiber and highly resistant to transfer to another piece of cloth by a rubbing action. This transfer of color from one piece of cloth to another which occurs when the two pieces of cloth are rubbed together is referred to as "crocking." Even though the process of dyestuff printing is expensive and requires several operations to effect the desired printing and setting of the dye on the printed textile materials, nevertheless such types of printed textiles have several advantages, particularly the advantage of being free of crocking. However, they are subject to the disadvantage that since the

2

coloring matter is of an organic origin, the coloring matter, as is characteristic of dyestuff prints, are not color-fast on exposure to sunlight and to ultra-violet irradiation.

In addition to dyestuff printing of textiles, there is the other process of printing on textiles, namely, that of "pigment printing" in which pigments of brilliant color can be deposited on the cloth. In pigment printing, there is employed a combination of a pigmentary coloring substance, which is substantially water and solvent insoluble, with a synthetic resin as a binder to attach the pigment particles to the cloth and also to act as a carrier for the pigment. Generally, this carrying medium for the pigment is in the form of an emulsion comprising the resin binder, solvent and water, made up in such a manner that the solvent and resin constitute the external or continuous phase and the water constitutes the inner or discontinuous phase, with the pigment homogeneously suspended throughout the emulsion. One of the advantages of employing pigment printing is the fact that during the process of the pigment printing, the operator applying the printing to the cloth can see the color in its final form as the cloth leaves the roll of the printing machine. Thus, if there is any adjustment to be made in any of the operations, such adjustments can be effected promptly to give the desired results. Moreover, pigment printing does not require the acid treatment (which may injure the cloth) necessary in dyestuff printing in order to set the coloration in the cloth. Generally it is only necessary after printing the pigment prints on the cloth to pass the latter over drying rollers, generally while employing elevated temperatures, and the cloth is then ready for packaging. In addition to being less costly than the dyestuff printing process, pigment printing is much less cumbersome to handle in the process of manufacture, the pigment prints are more brilliant in color than corresponding dyestuff prints of equal intensity, and what is even more advantageous, pigment printed cloths have the advantage of being more resistant to the fading action of sunlight and ultra-violet irradiation. However, pigment prints have a disadvantage in comparison with dyestuff prints in that they tend to crock to a much greater degree than do the dyestuff prints. Because of this latter disadvantage, pigment printing of textiles is not as widespread as dyestuff printing of textiles.

One of the objects of the present invention is to produce textile pigment prints having very low crock characteristics.

Another object of the invention is to set the resinous binder containing the pigment particles more rapidly and more firmly so that the crocking characteristics of the pigment are materially reduced.

In accordance with our invention, the textile materials which have been printed with pigmented printing compositions are subjected to irradiation with high energy electrons. In order to effect this treatment with the attendant reduction in crocking characteristics, it is essential in the printing process used for pigment printing of the textiles, that there be employed with the pigment printing compositions, organic compositions in the polymerizable or polymerized state which are capable of being converted to higher molecular weight materials as a result of the irradiation with the high energy electrons. These polymerizable or polymerized compositions, which will hereinafter be referred to as "electron-activatable bonding agents," are in addition to the resinous media or carrying agents for the pigments generally employed in pigment printing. Generally, such electron-activatable bonding agents comprise any substance which in the presence of high energy electrons will be converted to higher molecular weight compositions by means of the electrons.

Among the electron activatable bonding agents which may be employed are, for instance, monomeric polymerizable materials, as, for example, alpha methyl styrene, styrene, vinyl toluene, ethyl acrylate, n-butyl acrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol diacrylate, acrylonitrile, diethylene glycol maleate, diethylene glycol maleate adipate, etc. In addition to the individual monomeric composition described above, we can also employ mixtures of the aforementioned monomeric materials, as, for instance, mixtures of n-butyl acrylate and tetraethylene glycol dimethacrylate; mixtures of unsaturated alkyds with other copolymerizable monomers, as, for instance, mixtures of diethylene glycol maleate, diallyl phthalate and either vinyl toluene or styrene, mixtures of propylene glycol fumarate phthalate and either vinyl toluene, alpha methyl styrene, or styrene, mixtures of diethylene glycol maleate phthalate and either styrene or vinyl toluene, or alpha methyl styrene, etc., which are generically designated in the art as "polyester resins" and are commercially available under such trade names as Paraplex, Selectron, Vibrin, Laminac, Permafil, etc. The aforesaid unsaturated alkyds used with the copolymerizable monomeric compositions may be obtained by effecting reaction between a polyhydric alcohol, e.g., ethylene glycol, propylene glycol, dipropylene glycol, tetraethylene glycol, glycerine, pentaerythritol, sorbitol, etc., and an alpha unsaturated, alpha, beta dicarboxylic acid (or anhydride), as, for example, maleic acid or anhydride, fumaric acid, itaconic acid, citraconic acid, etc. The term "vinyl toluene" is intended to include all isomers thereof.

Additional materials which can be employed as electron activatable compositions convertible by high energy electrons to higher molecular weight products are, for instance, homopolymers of butadiene (e.g., butadiene-1,3), homopolymers of chlorobutadiene-1,3 (neoprene), copolymers of a butadiene, e.g., butadiene-1,3, and either styrene (GR-S) or vinyl toluene, copolymers of butadiene-1,3 and acrylonitrile (Hycar), natural rubber, etc. Generally, the polymeric compositions described above based on homopolymers and copolymers of diene derivatives are advantageously, although not necessarily, employed in the form of lattices.

A still further group of compositions which may be employed as the electron activatable material comprises such materials as, for example, nylon, polyalkyl acrylates (as described in Semegen Patents 2,412,475 and 2,412,476), and similar materials. Included among the electron activatable materials employed in the practice of the present invention are mechanical mixtures of the above-described polymeric compositions and mixtures of monomeric compositions with the polymeric materials, which, in the presence of the high energy electrons are converted to products of higher molecular weight. Additional examples of electron activatable materials which may be employed in the practice of the present invention may be found disclosed in Lawton and Schmitz application, Serial No. 291,541, filed June 3, 1952, now U.S. Patent No. 2,921,006, and in the copending applications of Elliott J. Lawton and Arthur M. Bueche, Serial Numbers 324,552, 324,554, now abandoned, and 324,555, now U.S. Patent No. 2,858,259, the latter three applications being filed December 6, 1952, and assigned to the same assignee as the present invention.

All the aforesaid electron activatable bonding agents described above may obviously be used in various stages of polymerization. The form of such agents may be, for instance, as emulsions, dispersions, solutions, or even in the dry, finely divided form, whereby the electron activatable bonding agent can be readily suspended in the pigment printing composition.

Generally, it is only necessary in the practice of our invention to employ suitable organic compositions either in a monomeric or polymeric form which in the presence of high energy electrons are converted to products of

higher molecular weight. In employing the aforementioned copolymeric materials as, for example, copolymers of butadiene and styrene, or butadiene and acrylonitrile, etc., the amount of butadiene employed may be varied widely and may range, for instance, from about 20 to 80 percent of the total weight of the copolymerizing ingredients, that is, copolymerizable ingredients comprising butadiene and styrene, butadiene and acrylonitrile, etc. The lattices of such polymeric materials are available on the market and details thereof may be found disclosed in the book "Modern Synthetic Rubbers" by Harry Barron, published by D. Van Nostrand Company, Inc., 2nd edition (1942).

Among the insoluble coloring agents or pigments which may be employed in the present invention are, for instance, highly colored chemical pigments such as phthalocyanine blue and green, cadmium red, benzidine yellow, various earth oxides, as for example, red iron oxide, prussian blue, carbon black, chrome green, etc. No limit is intended in the type of pigment which may be employed, the sole requisite being that it is one capable of being used in the pigment printing of fibrous sheet material, including textile materials. Reference to any of the art well known in connection with pigment printing of various fibrous materials, for instance, textiles, papers, etc., will reveal other examples of insoluble coloring agents or pigments which can be employed in the practice of the invention. The pigments, which may be of natural or synthetic origin, are generally employed as dispersions in a liquid phase comprising water of which mixture from about 10 to 30%, by weight, is the pigment.

In the textile printing system employed herein, we may use as the carrying agent for the pigment a water-in-oil or oil-in-water emulsion binders comprising, for example, an alkyd resin, a cellulose derivative, an amine resin, an oleagenous material, etc. These printing compositions may contain various emulsifying agents and other additives generally incorporated to contribute to the desired properties of the finished print. Among such resinous carrying agents which may be employed are, for instance, the above-mentioned alkyd resins, for example, modified or unmodified alkyd resins (exclusive of unsaturated alkyd resins mentioned above) obtained by effecting reaction between a polyhydric alcohol, many examples of which have been given above, and a polybasic acid free of olefinic polymerizable unsaturation. The above-mentioned resins when employed as carrying agents preferably comprise from about 1 to 35 percent, by weight, solids dispersed in a liquid. In preparing the carrying agent, various emulsifying or dispersing agents may be employed, examples of which may be mentioned, for instance, potassium alum, sodium sulfate, ammonium sulfate, as well as many other ionizable inorganic compounds.

Among the alkyd resins which may be employed in the preparation of the carrying agent may be those obtained by effecting intercondensation between a polyhydric alcohol and a polybasic acid or anhydride, either alone or with the usual oily modifying ingredients generally employed in the preparation of modified alkyd resins, said modifying ingredients being selected from the class consisting of non-drying oils, semi-drying oils, drying oils, fatty oils, fatty oil acids, and mixtures thereof, all the foregoing modifying agents being derived, for example, either from vegetable or animal sources, or produced synthetically. Examples of polyhydric alcohols (dihydric, trihydric, etc.) which can be used for this purpose are, for instance, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, trimethylene glycol, glycerine, pentaerythritol, sorbitol, mannitol, etc. Examples of polybasic acids (for instance, dicarboxylic, tricarboxylic, etc.) are, for instance, oxalic, malonic, succinic, glutaric, adipic, suberic, tricarballic, phthalic, isophthalic, terephthalic acid, diphenic, naphthalic, tetrachlorophthalic, etc. The anhydrides of these materials when obtainable may also be used. In addition to the polybasic

5

and polyhydric alcohols employed above, one may also use monohydric alcohols as modifying agents as, for instance, ethyl alcohol, propyl alcohol, etc.; monohydric alcohols boiling above 150° C. such as the alkyl ethers of diethylene glycol, e.g., methyl ethers of diethylene glycol, etc.; ethers of ethylene glycol, e.g., butyl Cello-solve, etc., may also be used to modify the properties of the oil-modified alkyd resin. Monocarboxylic acid may also be used to modify the properties, as, for instance, acetic acid, benzoic acid, etc.

Among the modifying oils (in the raw, heated, or blown state) which may be used in the preparation of oil-modified alkyd resins are, for instance, linseed oil, rapeseed oil, cottonseed oil, chinawood oil, castor oil (including raw castor oil and dehydrated castor oil), soya bean oil, perilla oil, oiticica oil, linseed oil acids, coconut oil fatty acids, ricinoleic acid, fatty acid glycerides, e.g. the glycerides of linoleic and linolenic acids, palmitic acid, oleic acid, stearic acid, fish oils, fish oil acids, etc. The amount of modifying oil ingredients may be varied widely and may range from about 5% to 70%, preferably from about 10 to 15%, by weight, of the total weight of the modifying oil, the polyhydric alcohol, the polybasic acids (or anhydride if it is used) present in the reaction mixture designed to make the alkyd resin.

The preparation of the alkyd resin is well known in the art and generally comprises heating a mixture containing the polyhydric alcohol, the polybasic acid, and the modifying oil at elevated temperatures ranging from about 150 to 200° C. for from about 2 to 12 hours or even longer, until the desired acid number of the reaction mixture is obtained. The acid number of the finally reacted material is preferably below 50, optimum results being obtained when the acid numbers are from about 4 to 10 or 20. Although equal molecular proportions of the polyhydric alcohol and the polybasic acid may be used in making the oil-modified alkyd resin, generally it is desirable to employ a slight excess of the polyhydric alcohol in order to cause the reaction to go more fully to completion. It will be understood, of course, by those skilled in the art that proportions other than of equal molecular quantities may be employed. For example, a larger molecular excess of polyhydric alcohol may be used if desired in order to obtain an alkyd resin of lower acid value.

In addition to the alkyd resin described above as carrying agents, one may also employ cellulose derivatives as, for example, ethyl cellulose, cellulose acetate, cellulose acetobutyrate, etc. The use of oil-modified phenolic resins as, for instance, oil-modified phenol-formaldehyde resins containing alkylated phenols as modifying ingredients to enhance the oil-solubility of the resin may also be employed without departing from the scope of the invention. Amine resin such as, for instance, urea-formaldehyde resins, butylated urea-formaldehyde resins, melamine-formaldehyde resins, aniline-formaldehyde resins, etc., also are intended to be included as carrying agents which may be used in the practice of the present invention.

In preparing a printing composition, it is generally desirable to form a solution of the alkyd resin in a solvent therefor, for instance, mineral spirits, toluene, etc., or mixtures of such solvents so that there is preferably present about 3 to 15% resin solids, based on the total weight of the resinous carrier solution. Thereafter, the carrier solution is then emulsified with water employing the usual emulsifying agents as, for instance, potassium alum, for the purpose. This mixture is subjected to milling in a colloid mill to form a water-in-oil emulsion. Thereafter, the electron activatable bonding agent is added, this activatable bonding agent advantageously being employed in the form of a water emulsion or dispersion so that it can be readily blended with the suspension or dispersion of the carrier resin. When a homogeneous mixture of the carrier resin and the electron activatable composition is formed, the desired pigment, which is also preferably

6

dispersed in water, is added. The entire mixture is subjected to high speed mixing to form a uniform paste.

Obviously, when monomeric polymerizable compositions are employed as the electron activatable bonding agent, other techniques may be required in order to blend the latter with the carrying resinous agent. Generally, when, for instance, n-butyl acrylate or tetraethylene glycol dimethacrylate is employed, it may be desirable to dissolve the latter in a solvent and form an emulsion thereof in water which can be readily admixed with the carrier resin composition.

As will be apparent to persons skilled in the art, the proportions of the various ingredients used to carry the pigments may be varied within wide limits without departing from the scope of the invention. With specific regard to the carrying agent, a ratio of ingredients which is satisfactory comprises the following ingredients by weight:

		Parts
20	Resinous portion of carrying agents (e.g. alkyd resins, cellulose derivatives, etc.)	1 to 7
	Water	20 to 80
	Solvent	15 to 35

A pigment printing composition which can advantageously be used in the practice of the present invention, but to which we do not intend to be limited, comprises the following essential ingredients in the stipulated parts, by weight,

		Parts
30	Carrying agent (including resinous binder and liquid phase)	40 to 70
	Electron activatable bonding agent (solids portion)	10 to 40
35	Dry pigment	1 to 6

Obviously, the proportions of the ingredients may be varied widely depending upon such factors as the application for which the printing pigment is intended, the ingredients employed in the preparation of the pigment printing composition, etc.

After the textile material has been treated with the pigmented printing composition, it is advantageous to pass the treated cloth over heated drying rolls or through heated ovens whereby the water and solvent present on the cloth are volatilized. For this purpose, temperatures ranging from about 75° to 150° C., depending on the type of electron activatable material, solvent present, etc., are advantageously employed for times ranging e.g., from a few seconds to about 2 to 5 minutes or more.

Thereafter, the dried printed textile material is passed through a beam of high energy electrons for the purpose of irradiating the printed portion of the textile material. High voltage accelerating apparatus 1 adapted for such purpose is illustrated in the accompanying single figure, and may be of the type disclosed in U.S. Patent 2,144,518, Westendorp, January 17, 1939, and assigned to the assignee of the present invention. As shown in the accompanying drawing, this apparatus comprises a resonant system having an open-magnetic circuit inductance coil (not shown) which is positioned within a tank 2 and energized by a source of alternating voltage to generate a high voltage across its extremities. At the upper end (not shown) of a sealed-off, evacuated, tubular envelope 3 is located a source of electrons which is maintained at the potential of the upper extremity of the inductance coil, whereby a pulse of electrons is accelerated down envelope 3 once during each cycle of the energizing voltage when the upper extremity of the inductance coil is at a negative potential with respect to the lower end. Further details of the construction and operation of the high voltage accelerating apparatus may be found in the aforementioned Westendorp patent and in "Electronics," vol. 17, pp. 128-133 (December 1944).

To permit utilization of the high energy electrons accelerated down envelope 3, there is provided an elon-

7

gated metal tube 4, the upper portion 5 of which is hermetically sealed to tank 2, as illustrated, by any convenient means such as silver solder. The lower portion 6 of tube 4 is conical in cross section to allow an increased angular spread of the electron beam. The emergence of high energy electrons from tube 4 is facilitated by an end-window 7 which may be hermetically sealed to tube 4 by means of silver solder. End-window 7 should be thin enough to permit electrons of desired energy to pass therethrough but thick enough to withstand the force of atmospheric pressure. Stainless steel of about 0.002 inch thickness has been found satisfactory for use with electron energies of about 230,000 electron volts or greater. Beryllium and other materials of low stopping power may also be employed effectively. By forming end-window 7 in arcuate shape as shown, greater strength for resisting the force of atmospheric pressure may be obtained for a given window thickness. Desired focusing of the accelerated electrons may be secured by a magnetic-field generating winding 8 energized by a source of direct current 9' through a variable resistor 9.

As further shown in the accompanying drawing, in the treatment of the pigment-printed sheet material, for example, textile material 10, the latter is supported by means of a mandrel 11 revolving in the direction of the shown arrows so that the pigment-printed cloth unrolls and subsequently passes in the path of electrons emerging from end-window 7 as illustrated. The high energy electrons penetrate the cloth as it passes underneath thereby to a depth dependent upon their energy, and effect the desired changes in the properties of the pigment printing described above. In order to permit irradiation of the sheet material throughout its width, the source of high energy electrons may be mounted on a laterally moving apparatus (not shown) so as to allow the end-window 7 to oscillate back and forth as indicated by arrows 12 and 13 across the width of the sheet material in such a manner that the entire surface of the sheet material being treated passes at one time or another under the end-window 7 and is subjected to the high energy electrons. Another method for irradiation comprises moving the sheet material laterally while the source of high energy electrons is fixed in one position, this again effecting irradiation of the entire width of the cloth. Alternatively, a battery or series of sources of high energy electrons similar to that described in FIG. 1 is distributed in such a fashion that each end-window covers a contiguous portion of the sheet material being treated and all the sheet material being passed under the end-windows is at one time or another subjected to the high energy electrons emanating from the end-windows. If the sheet material is in the form of a strip material, which is generally the case, it is advantageously passed continuously under end-window 7 at a velocity selected to give the desired irradiation dosage and rolled up again by means of another roll on a mandrel.

Other expedients for obtaining the irradiation of the pigment-printed textile materials will be apparent to those skilled in the art. In certain instances it may be desirable to effect irradiation by the high energy electrons in an atmosphere of nitrogen, argon, helium, krypton, or xenon, etc.

The improvements in the properties of the pigment printed textile material, particularly the crocking properties thereof, may be realized employing the requisite dosage of high energy electrons which are generally stated to be defined as roentgen units. A roentgen unit is usually defined as the amount of irradiation that produces one electrostatic unit of ion pairs per milliliter of dry air under standard conditions and, as employed here, refers to the amount of electron radiation measured with an air equivalent ionization chamber at the position of the upper surfaces of the pigment-printed textile material. It has been found that measurable improvements in the crocking of the textile materials can be produced at irradiation

8

doses as low as about 1×10^6 R. For example, dosages of from 1×10^6 R. to 5×10^6 R. are from 10 to 20 times better than non-irradiated samples; dosages above 2×10^6 R. will almost completely eliminate crocking of textile materials printed with various kinds of pigmented resins containing the "electron activatable" binder in combination therewith. It will, of course, be apparent to those skilled in the art that the exact irradiation dosage employed in each case will vary depending on many factors and the applicants do not intend to be limited to any particular limit or ranges. Obviously, irradiation dosages below 1×10^6 R. and higher than 5×10^6 R. may be employed without departing from the scope of the invention. Each application will recommend the proper irradiation dosage required. The temperature at which the irradiation is carried out is not critical as long as the temperature used does not adversely affect the printed sheet material or in any way interfere with the attainment of the desired results. Generally, it is desirable that the irradiation dosage employed be sufficient to convert the pigment-printed textile material to a substantially non-crocking state.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

Example 1

In this example, a pigment-containing printing composition was prepared as follows. The carrying agent was prepared by mixing together, on a weight basis, 20 parts of a 50% solids mineral spirits solution of an alkyd resin derived from the co-reaction product of maleic anhydride, tall oil acids, sorbitol, pentaerythritol, diethylene glycol, and oiticica oil, 200 parts of a petroleum solvent, specifically mineral spirits, 300 parts water and 5 parts of potassium alum. This mixture was then milled on a colloid mill to form a water-in-oil emulsion. About 60 parts of the above-described carrying agent were mixed with (a) 30 parts of an electron activatable bonding agent, specifically a butadiene-styrene copolymer dispersion in water in which the butadiene comprised about 80% of the total weight of the butadiene and styrene prior to copolymerization and in which dispersion, the butadiene-styrene copolymer solids comprised about 50%, by weight, and (b) 10 parts of a pigment-water dispersion of which 20% was dry pigment solids comprising phthalocyanine blue. The mixing of the ingredients was accomplished by dispersing the pigment in the carrying agent and thereafter adding the electron activatable bonding agent, and the ingredients thoroughly mixed by means of a high speed stirrer. The pigmented printing composition was then deposited on cotton cloth employing a conventional intaglio rotary print machine. The printed cloth was then divided into three parts. One part was employed as a control in which no further treatment was given. Part 2 was heated at 260° F. for about six minutes. Part 3 was irradiated with high energy electrons in an electron beam by passing the printed cloth through the beam of electrons so that it received a total dose of about 3×10^6 R. in all portions of the cloth. Each printed part was then tested for crocking using the standard test method entitled "Color Fastness to Rubbing (Crocking)," 8-52, referred to on page 106 of the 1952 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists, published by the American Association of Textile Chemists and Colorists at Lowell, Massachusetts. This test method differentiates four classes of color transfer as a result of rubbing one piece of printed cloth over another piece of printed cloth. These are:

- Class 1—greatest color transfer
- Class 2—considerable color transfer
- Class 3—very little color transfer
- Class 4—virtually no color transfer

The portions of the printed fabric when tested according to the aforementioned test 8-52 showed the following results:

Part 1 (no treatment), test result—class 2

Part 2 (heat treatment), test result—class 2 (but slightly better than part 1)

Part 3 (irradiated in electron beam), test result—class 4

As a further control and to illustrate the necessity of having an electron-activatable composition in the pigment printing material, a printing composition was prepared by intimately mixing together 90 parts, by weight, of the carrying agent described above, and 10 parts of the water pigment dispersion described above. The printing medium was deposited on cotton cloth from a conventional intaglio rotary printing machine and this printed cloth was divided again into 3 parts and each part treated as described above for parts 1, 2 and 3. As a result of the treatments mentioned above, testing of the various portions of cloth in accordance with the standard test referred to above showed that all three parts fell into class 1. It is clearly apparent that the combination of an electron-activatable bonding agent with the irradiation by high energy electrons is necessary in order to achieve the low crocking properties of the pigment-printed cloth.

Example 2

In this example, a pigmented printing composition was prepared similarly as was done in Example 1 with the exception that in place of the copolymer of butadiene and styrene, there was employed an equivalent amount of a water emulsion containing finely divided polyacrylonitrile. When cloth was printed with such a pigmented composition and irradiated with high energy electrons as described above in Example 1, approximately the same improved results (class 4) were realized as to crocking.

It will, of course, be apparent to those skilled in the art that instead of employing the carrying agent described above, other carrying agents (e.g., castor oil-modified glyceryl phthalate resins), many examples of which have been given, may also be used without departing from the scope of the invention. In addition, instead of the particular polymeric material employed as the electron activatable bonding material, other electron activatable materials, including polymerizable monomeric compositions, examples of which have also been given previously, may be used. Obviously, other pigments in place of the phthalocyanine pigment may be used and the proportion of all the ingredients may be varied widely as, e.g., in accordance with the suggested formulations mentioned previously.

It will be readily realized that other forms of electron accelerating apparatus may be employed instead of the high voltage apparatus described in the accompanying figure. For example, linear accelerators of the type described by J. C. Slater in the "Reviews of Modern Physics," vol. 20, No. 3, pp. 473-518 (July 1948), may be utilized, or electrostatic accelerators of the type described in Van de Graaff U.S. Patent 1,991,236. In general, the energy of the electrons employed in the practice of the invention may range from about 50,000 electron volts to 20 million electron volts or higher, depending upon the depth to which it is desired to irradiate the materials undergoing treatment. To decrease wasteful energy absorption between the point of exit of electrons from the accelerating apparatus and the pigment-printed fibrous materials, a vacuum chamber having thin entrance and exit windows may be inserted in the space.

By means of our invention, it is possible to print with pigments by various printing techniques (e.g., intaglio, offset, screen, etc., transfer methods) on various sheet fibrous materials, e.g., textile materials, various types of paper, etc. Advantage can now be taken of printing textile materials by the lower cost pigment print-

ing method and at the same time realize the advantages inherent in dyestuff printing, namely, non-crocking properties and higher degree of color fastness to light. By means of our method of treating textile materials with pigmented prints and thereafter irradiating the treated textile materials, it is possible to obtain brilliantly colored cloth of all types which can be employed in applications requiring resistance to elements including rain, sun, etc., while at the same time being substantially free of any crocking disadvantages. The irradiated pigment-printed fibrous sheet materials herein described with their low crocking properties can be used to make wrapping paper, paper and cardboard containers, awnings, garden furniture using the herein described fabrics for seats and backrests, clothes, etc.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The process for improving the crocking and color-fastness properties of pigment-printed surfaces of fibrous sheet material in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight composition, the said resinous carrying agent being selected from the class consisting of saturated alkyd resins, oil-modified saturated alkyd resins, ethyl cellulose, cellulose acetate, cellulose acetobutyrate, oil-modified phenol-formaldehyde resins, urea-formaldehyde resins, butyrate urea-formaldehyde resins, melamine-formaldehyde resins, and aniline-formaldehyde resins, the said binder being selected from the class consisting of styrene, vinyl toluene, ethyl acrylate, n-butyl acrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol diacrylate, acrylonitrile, diethylene glycol maleate, diethylene glycol maleate adipate, mixtures of unsaturated alkyd resins with other copolymerizable monomers, homopolymers of butadiene, homopolymers of chlorobutadiene, copolymers of butadiene-1,3 and styrene, copolymers of butadiene-1,3 and vinyl toluene, copolymers of butadiene-1,3 and acrylonitrile, natural rubber, and mixtures of the aforesaid binders, which process comprises (1) carrying out the pigment printing on the aforesaid sheet material employing the above-described pigmented printing composition in the form of an aqueous suspension, (2) drying the aforesaid sheet material and (3) thereafter irradiating the pigment-printed surface with high energy electrons with an irradiation dose of at least 1×10^6 R. while said sheet material is being passed through the electrons, the said high energy electrons being allowed to impinge on the sheet material to convert the above-mentioned binder to a higher molecular weight composition.

2. The process for improving the crocking and color-fastness properties of a dried, pigment-printed surface of textile sheet material in which the pigment printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent for the pigment comprising an alkyd resin, and from 10 to 40 parts of a binder for the pigment comprising an electron-activatable composition, which in the presence of high energy electrons is converted to a higher molecular weight composition, the said electron-activatable composition being selected from the class consisting of styrene, vinyl toluene, ethyl acrylate, n-butyl acrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol diacrylate, acrylonitrile, diethylene glycol maleate, diethylene glycol maleate adipate, mixtures of unsaturated alkyd resins with other copolymerizable monomers, homopolymers of butadiene, homopolymers of chlorobutadiene, copolymers of butadiene-1,3 and styrene, copolymers of butadiene and vinyl toluene, copolymers of butadiene-1,3 and acrylonitrile, natural rubber, polyalkyl acrylate, and mixtures of the aforesaid electron-activatable compositions,

which process comprises subjecting the aforesaid pigment-printed textile material to irradiation with high energy electrons with a dose of at least 1×10^6 R.

3. The process as in claim 2 in which the electron-activatable material comprises a mixture of ingredients comprising an unsaturated alkyd resin and styrene.

4. The process as in claim 2 in which the electron-activatable material is a polyalkyl acrylate.

5. The process for improving the crocking and color-fastness properties of pigmented surfaces of textiles in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent selected from the class consisting of saturated alkyd resins, oil-modified saturated alkyd resins, ethyl cellulose, cellulose acetate, cellulose acetobutyrate, oil-modified phenol-formaldehyde resins, urea-formaldehyde resins, butyrate urea-formaldehyde resins, melamine-formaldehyde resins, and aniline-formaldehyde resins, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight composition comprising a copolymer of butadiene and styrene, which process comprises subjecting the above-mentioned pigment-printed textile to irradiation with high energy electrons with a dose of at least 1×10^6 R.

6. The process for improving the crocking and color-fastness properties of pigmented surfaces of textiles in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent selected from the class consisting of saturated alkyd resins, oil-modified saturated alkyd resins, ethyl cellulose, cellulose acetate, cellulose acetobutyrate, oil-modified phenol-formaldehyde resins, urea-formaldehyde resins, butyrate urea-formaldehyde resins, melamine-formaldehyde resins, and aniline-formaldehyde resins, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight composition comprising polyacrylonitrile, which process comprises subjecting the above-mentioned pigment-printed textile to irradiation with high energy electrons with a dose of at least 1×10^6 R.

7. The process for improving the crocking and color-fastness properties of pigmented surfaces of textiles in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent selected from the class consisting of saturated alkyd resins, oil-modified saturated alkyd resins, ethyl cellulose, cellulose acetate, cellulose acetobutyrate, oil-modified phenol-formaldehyde resins, urea-formaldehyde resins, butyrate urea-formaldehyde resins, melamine-formaldehyde resins, and aniline-formaldehyde resins, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight composition comprising n-butyl acrylate, which process comprises subjecting the above-mentioned pigment-printed textile to irradiation with high energy electrons with a dose of at least 1×10^6 R.

8. The process for improving the crocking and color-fastness properties of pigment-printed surfaces of textile sheet material in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent comprising an alkyd resin, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight composition comprising polyacrylonitrile, which process comprises subjecting the above-mentioned pigment-printed textile material to irradiation with high energy electrons with a dose of at least 1×10^6 R.

9. The process for improving the crocking and color-

fastness properties of pigment-printed surfaces of textile sheet material in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent comprising an alkyd resin, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight polymeric composition comprising n-butyl acrylate, which process comprises subjecting the above-mentioned pigment-printed textile material to irradiation with high energy electrons with a dose of at least 1×10^6 R.

10. The process for improving the crocking and color-fastness properties of pigment-printed surfaces of fibrous sheet material in which the pigmented printing composition comprises (1) a pigment, (2) a resinous carrying agent for the pigment selected from the class consisting of saturated alkyd resins, oil-modified saturated alkyd resins, ethyl cellulose, cellulose acetate, cellulose acetobutyrate, oil-modified phenol-formaldehyde resins, urea-formaldehyde resins, butyrate urea-formaldehyde resins, melamine-formaldehyde resins, and aniline-formaldehyde resins, and (3) a binder for the pigment convertible by high energy electrons to a higher molecular weight composition, the proportions of the aforesaid ingredients being sufficient to attach the pigment particles to the fibrous sheet material, the said binder being selected from the class consisting of styrene, alpha methyl styrene, vinyl toluene, ethyl acrylate, n-butyl acrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol diacrylate, acrylonitrile, diethylene glycol maleate, diethylene glycol maleate adipate, mixtures of unsaturated alkyd resins with other copolymerizable monomers, homopolymers of butadiene, homopolymers of chlorobutadiene, copolymers of butadiene-1,3 and styrene, copolymers of butadiene-1,3 and vinyl toluene, copolymers of butadiene-1,3 and acrylonitrile, natural rubber, polyalkyl acrylates, and mixtures of the aforesaid binders, which process comprises subjecting the above-mentioned pigment-printed sheet material to irradiation with high energy electrons with a dose of at least 1×10^6 R.

11. The process for improving the crocking and color-fastness properties of pigment-printed surfaces of textile sheet material in which the pigmented printing composition comprises, by weight, from 1 to 6 parts of a pigment, from 40 to 70 parts of a resinous carrying agent comprising an alkyd resin, and from 10 to 40 parts of a binder for the pigment convertible by high energy electrons to a higher molecular weight composition comprising a copolymer of butadiene and styrene, which process comprises subjecting the above-mentioned pigment-printed textile material to irradiation with high energy electrons with a dose of at least 1×10^6 R.

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