

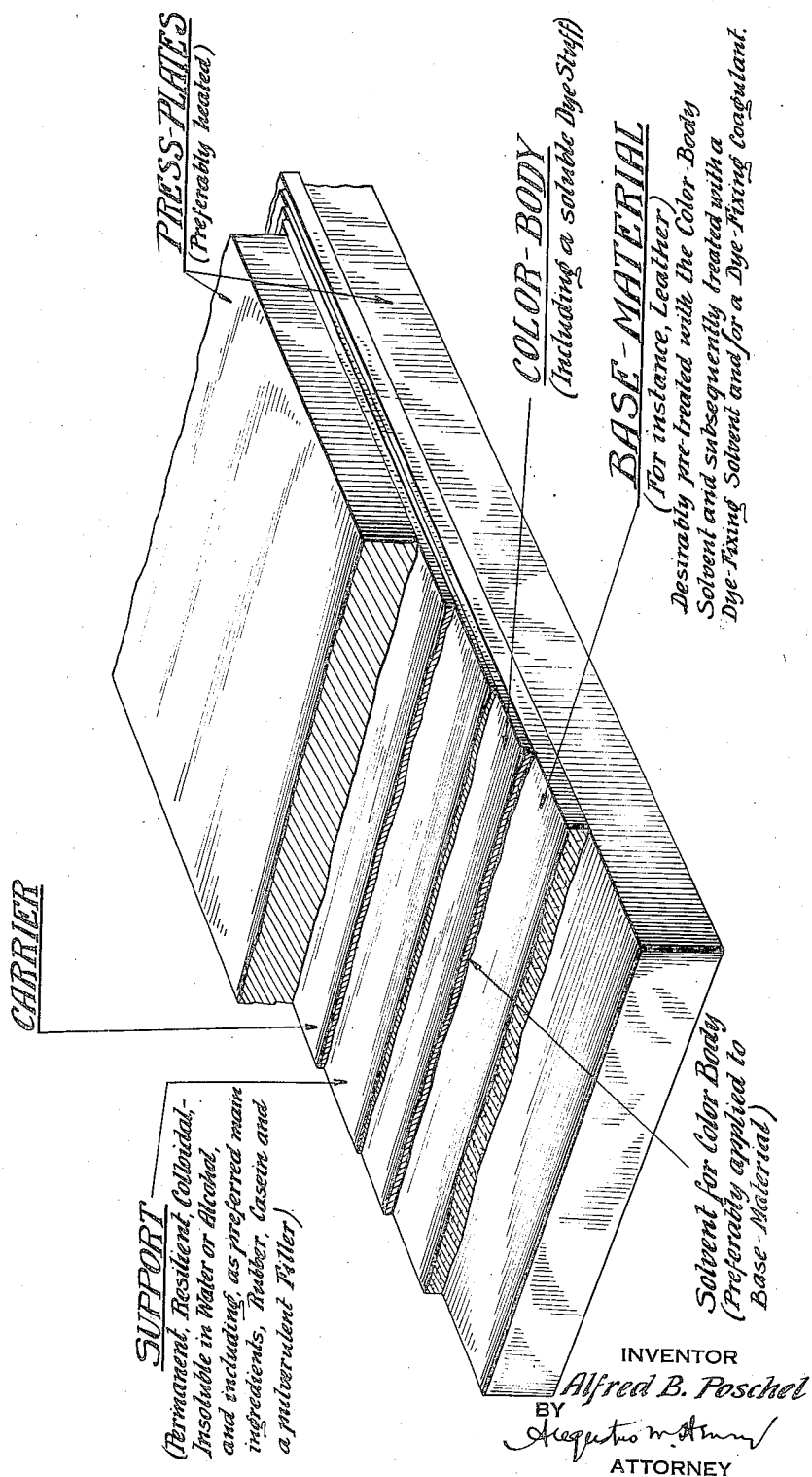
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ORNAMENTATION

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This invention relates to the dyeing, coloring or decorating of fibrous materials, particularly leather, as well also as other absorbent and/or fibrous material by transfer.

5 Among the objects of the invention is to provide as a new article of manufacture a specially constructed transfer-sheet (or web), including a suitable carrier as a paper sheet (or web), a permanent resilient non-water-soluble and non-alcohol-soluble coating, and, overlying the latter, a solid or open-work layer of permanently soluble colloidal coloring matter. Said resilient coating will hereinafter be referred to as the support, and said layer of coloring matter will be hereinafter referred to as the color-body.

By transfer is meant the transferring of a previously spread color-body from a temporary carrier to a base material to be processed by a dyeing, coloring or other decorative treatment derived from the application of said color-body thereto.

According to the present invention, a novel and valuable method is provided whereby a desired base material is dyed, colored or decorated, that is, processed, by the use of such color-body in combination with pressure and/or solvent without necessarily having to employ specially applied heat and without necessarily having to employ moisture or water unless the color-body include water-soluble dye and hence water is the solvent,—so that the transfer-sheet may finally be removed by a mere stripping-off operation.

By dyeing, coloring or decorating is meant any varying of the previous color, hue, tint or shade of the material, including black and white as well as true colors, whether such dyeing, coloring or decorating be continuous over its extension plane and/or one color, or interrupted and/or varicolored so as to produce patterns of any kind, as found in nature or otherwise.

According to the invention, more specifically, a transfer-sheet is provided including a paper or other coatable carrier, and, on said carrier and as a secondary subdivision of the transfer-sheet, a permanent, resilient, non-water-soluble and non-alcohol-soluble colloidal support. This support preferably includes emulsified rubber, casein and zinc stearate as typical main constituents; and the same, in liquid form, is desirably coated or otherwise suitable spread, over the surface of said carrier to form after drying a strong or tough layer or film thereon inseparably bonded thereto. The function of said support is first to receive and later to release the characteristic design and/or color of the color-body, to prevent

capillary attraction by the fibres of the carrier (when of paper) relative to the color-body material, and to provide under the influence of suitable pressure a desired slight adhesion between the support and the processed material. By processed material is meant any material, as leather, being decorated, colored, or otherwise marked, by release thereto of coloring material from the transfer-sheet.

Thus according to the invention, a transfer-sheet or web is provided having as a tertiary subdivision, placed on the surface of said secondary subdivision or support, a permanently soluble and colloidal color-body. This color-body is spread and dried on the support, as by a single or several coating and/or printing operation or operations, to provide a solid color layer or a multi-colored pattern or picture. According to the invention, further, said color-body has a variable composition to meet the special requirements of the material to be dyed, colored or decorated and appropriate to the particular means employed to establish the color-body on the support. Such color-body may include a water-soluble-dye such as naphthol blue black and/or an alcohol-soluble dye such as luxol fast black and/or an oil-soluble-dye such as Deigy oil black #14 and/or a pigment, and a suitable vehicle and/or a suitable solvent and/or a suitable plasticizer, the mixture varying in viscosity from a heavy paste to a thin liquid, and being, preferably, water-soluble or alcohol-soluble or oil-soluble. As an important advantage, the present invention permits the use of non-fixed dyes in lithographic printing, which so far has been considered impractical; this following from the fact that the components of the color-body are intermixed yet held in finest subdivision, the ultimate material being truly colloidal and not crystalline after becoming spread and set, and the resulting layer being finally homogeneous, smooth and non-crumbling. Such a physical condition of the spread and set color-body is believed essential to commercially successful working of the method of the present invention as hereinabove stated.

Said method, employable as aforesaid for a dyeing, coloring or decorating of a suitable material to be processed, and involving the use of a previously spread and soluble color-body of the novel and valuable kind already explained so that the coloring matter thereof (wholly or partially as desired) is released to the processed material by pressure and/or solvent, has also the important advantage that the transfer-sheet carrying said color-body on the resilient sup-

port may be finally removed from the processed material by a stripping-off operation merely; that is, specially-applied heat need not be used for the color transfer, and specially applied water need not be used for the stripping-off operation. As to the color transfer, the pressure employed is rather high, as hereinafter particularized. Desirably, the requisite pressure is attained by squeezing the transfer-sheet and the material to be processed between the platens of a hydraulic press,—although it is well then to operate the press in such a way that the color-body will be held in suspension over the material to be processed and lowered to contact the same flatwise all over coincidentally with the final closing of the press, thereby to prevent any remotely possible chance of smudging even when very delicate and multi-color patterns are being transferred. Any smudging is largely insured against, however, both during the transfer step and during the stripping-off step, by the novel property of the special color-body support of the present invention whereby such support has a tendency to adhere somewhat to the material being processed.

The invention further has the aim of providing a practical working method for the after-treatment of a base material, dyed, colored or decorated by transfer of coloring matter from a color-body of the kind aforesaid, which method may involve, if desired, the fixing of said transferred coloring matter by coagulating material preferably albumin, spread over the surface of the base material after removal of the transfer-sheet.

The present invention will be clearly understood and the foregoing objects more fully appreciated, and various other objects and advantages thereof will become manifest, from the following detailed description of certain preferred ways of practicing the invention, one specific way or example of which is illustrated in the accompanying drawing.

Desirably, the new transfer-medium is prepared by providing a suitable material in web or sheet form to act as a practicable carrier for the coating to establish the new support. Paper is the most economical and otherwise satisfactory material for this purpose. A paper which is well sized and has a fairly smooth surface is preferred; very absorbent paper and paper of poor tensile strength is not recommended. The thickness is variable, but a thickness of about three thousandths of an inch has given good results.

The paper chosen as said carrier is then coated with a layer of special material; said material being applied preferably in liquid form and by means of a paper-coating machine, against one side of said carrier, to lay or build up thereon, by one or more coating operations, a film or integument of the desired thickness (one to two thousandths of an inch having been found satisfactory), such film or integument to form when dried the support for the color-body.

This special material, which in liquid state is an emulsion, forms in its dry state a colloidal, smooth and permanent, resilient layer. This layer, practically insoluble in water, alcohol and oil, is well adapted to serve as a temporary and neutral support for a color-body having coloring matter pursuant to the invention. Said support is impermeable and prevents capillary attraction by the carrier even when fibrous (as paper) relative to the coloring matter of the

color-body. Being dry, the support persists in inseparable bond with said carrier, and subsists as a smooth and permanently resilient layer which has a somewhat velvety feel and which is practically non-tacky. Yet under the influence of pressure this layer takes on a temporarily increased adhesiveness, which is desired. Its neutral behavior permits it to receive and to release coloring matter very well, and it preserves its working qualities permanently, so that it may be spread and dried independently and in advance.

The following is a useful formula for the preparation of a coating material for establishing the support.

	Parts
Rubber latex.....	40
Dry casein.....	10
Zinc stearate.....	5
Water	50-100
Paraffin emulsion.....	5
Formalin	2
Triethanolamine	3

Rubber is the most important constituent because of its permanently resilient quality. Rubber latex is preferred since it contains rubber in a highly subdivided state, emulsifies easily with other materials, and is commercially available. It has been found that for the rubber latex there might be substituted dry rubber or caoutchouc, vulcanized and redissolved and then emulsified, or even synthetic rubber and other substitutes, but because of its simple handling latex is recommended. However, the use of rubber alone has given relatively poor results in the present connection. It has a tendency to stick too firmly to the processed material and to peel from the carrier, during the stripping-off operation.

This objection I have also overcome, by the use of casein. I find that the addition of a certain amount of casein insures a firm bond of the support to the carrier, without destroying its resilience. Other materials, i. e., albumin, gelatine, glue, apparently may be substituted for the casein to increase clingability of the support to the carrier, but casein seems to be most satisfactory.

The emulsifying of rubber and casein increases rather the tackiness of the resulting layer. By the incorporation of a filler, preferably of a pulverulent nature, such as zinc stearate, said tackiness can be controlled to the desired degree. While for such control I may use aluminum stearate or talcum as a substitute, zinc stearate has been found most suitable for the purpose.

Water, aside from its use as a solvent, is used to control as desired the degree of viscosity of the emulsified material.

The addition of a certain amount of paraffin emulsion has been found to improve the release of coloring matter from the support, and also to oppose excessive tackiness in cooperation with zinc stearate. Other emulsions of fatty matter could be substituted, i. e., castor oil emulsion, or sulphonated oils. However, paraffin emulsion is recommended as apparently most desirable.

Formalin (formaldehyde) is used as a preservative against putrefaction, and, as well, as a coagulator, to insure insolubility. Formalin is apparently the most suitable material for this purpose.

Triethanolamine is preferred as an emulsifying agent and as a stabilizer for the resulting emulsion. Other emulsifying agents could be used for the same purpose, i. e., ammonia, emulsone; but

triethanolamine is recommended because it gives very stable emulsions.

Desirably, these materials are homogenized by mechanical means, preferably a colloid mill, in such manner as to form a perfect and stable emulsion which may be preserved without loss of its working quality for a reasonable time.

The coating material prepared in the way described is then ready to be coated on said carrier.

For this work a suitable paper coating machine is preferably used. Generally, one single coating is sufficient; but may be repeated if desired. To warrant best results, this coating must be perfectly even. Care must be taken that the coated material is allowed to set or dry before it is rolled or piled up.

It is advantageous to season said carrier, after being coated, for from one to several days.

After being coated and seasoned, said support on the carrier presents a smooth, velvety and resilient surface, which is practically insoluble in all ordinary solvents, like water, alcohol or oil. It makes an ideal printing surface, which by a cushion-like and velvety effect takes up more coloring matter, as for example printing ink up, and better than ordinary paper. Pursuant to the invention as already stated, this support is intended to serve only as a temporary support for a color-body; it must, therefore, under certain conditions, separate itself easily from said coloring matter. This condition is fulfilled by the permanent resilience and impermeability of the layer forming the support, and the secure bond of the latter to the carrier, the support being further advantaged by its neutral and somewhat velvety and fatty surface. The thus created support is substantially unitary with the carrier, and these two elements as subdivisions of a transfer-sheet or web, present a new and valuable article of manufacture in the transfer art.

The further steps of manufacturing such transfer-sheet or web are alternative, and depend on the nature of the proposed dyeing, coloring or decorating, and the materials to be processed.

Suppose plain solid colors are desired similar to those obtained by vat-dyeing: the simplest and least expensive way to produce the color-body is to prepare a varnish-like and perfectly homogenized mixture, comprising dyestuff and/or pigments, solvent, vehicle, binder and plasticizer, and to coat said varnish-like colored mixture, preferably by means of a coating machine, on said support. It is desirable that the color-body be perfectly even. After setting and seasoning, it forms a permanently soluble layer of coloring matter in a colloidal state, and from now on the new transfer-sheet or web is ready for immediate use or for storage away for later application.

The following is an illustrative formula for a mixture of the kind last described, adapted to produce a water-soluble color-body, and consequently including the use of water as an impregnating solvent for the transfer:

	Parts
Basic dyestuff such as basic black S. B. Newport.....	24
Acetic acid.....	18
Water.....	48
Albumin dry.....	3
Gum arabic.....	3
Molasses.....	2
Triethanolamine.....	2

In case an alcohol-soluble mixture is preferred, the following formula is very suitable. Its use requires, naturally, the use of an alcoholic impregnating solvent for the transfer:

	Parts
Luxol dyestuff (Dupont).....	25
Diethylene glycol ethyl ether.....	5
Methyl alcohol.....	10
Cumar resin.....	5
Blown castor oil.....	3
Shellac dry.....	2
Ethylene glycol ethyl ether.....	30
Ethylene dichloride.....	20

The resinous constituents of this formula may be replaced by nitrocellulose or acetate cellulose.

For the latter a suitable solvent should be included. The following is a formula of this kind.

	Parts
Luxol dyestuff.....	25
Methyl alcohol.....	15
Cellulose acetate.....	5
Acetone.....	20
Ethyl lactate.....	10
Toluol.....	20
Gum elemi.....	2
Tricresyl phosphate.....	3

Its use involves the employment of a cellulose acetate solvent as an impregnating solvent, i. e., acetone, for the transfer.

In case that more coverage is desired than dyes give, a certain amount of a suitable pigment or pigments, say 5-10 parts or more, may be included. The following formula is of this type. Its use requires an alcoholic impregnating solvent for the transfer:

	Parts
Nigrosine alc. sol.....	20
Carbon black.....	5
Methyl alcohol.....	15
Sandarac resin.....	5
Denat. alcohol.....	25
Butyl alcohol.....	5
Petrol. ether.....	20
Dibutylphthalate.....	5

It is understood that these formulae can be greatly varied to suit special cases. The mixtures resulting from the above formulae are concentrated and may be diluted for use. Grinding, dissolving and mixing must be done very thoroughly. Care must be taken to prevent recrystallization of the dyes and the gelatinizing of the mixtures which might occur.

However, when the dyeing, coloring or decorating, instead of involving plain solid color shades, is performed in regard to single or multi-colored patterns, or even pictures, to be transferred, the color-body incorporating such a pattern or picture on the surface of the special support is best produced by printing, which is to be understood as including the use of photomechanical reproduction methods for the production of printing surfaces. For this purpose, type-printing and rotogravure-printing are suitable methods. Especially is the latter useful to produce endless patterns in webs. For these printing methods, dyestuff inks can be used without great technical difficulties. The following is an illustrative formula for an ink dyestuff for rotogravure to be used in this connection. Its use involves

the use of an alcoholic impregnating solvent for the transfer:

	Parts
5 Dyestuff alcoholic sol -----	30
Methyl alcohol -----	20
Gum elemi -----	5
Diatomaceous earth -----	5
Ethylene dichloride -----	20
10 Carbon tetrachloride -----	20

For the production of more elaborate color effects the use of lithographic printing methods is very desirable. But, in connection with the present process, lithographic printing presents a special problem. The use of linseed oil varnish, which is the only practical vehicle for lithographic printing ink, is not suitable in this case. Linseed oil dries by oxidation and forms in dry state a gel, which is not reversible to a true liquid. Consequently, the ready dissolution and liberation of dyes incorporated in such a layer of linseed oil varnish by the action of an impregnating solvent, which is essential in this process, is not possible. Linseed oil and similar drying oils must, therefore, be eliminated as the, or from the, vehicle for coloring matter in connection with this process.

I have found that certain synthetic resins, i. e., coumarone, chlorinated diphenyl, polymerized terpenes, in a proper state of condensation, and in combination with non-drying oils and essential oils, are suitable to be used as vehicles for non-fixed dyes for the preparation of inks for lithographic printing. The resulting varnishes or vehicles are either non-drying or dry by evaporation and condensation, and are permanently soluble.

The formulation of such a varnish or vehicle, having the general working qualities of linseed oil varnish, which are indispensable for lithographic printing, is very important, and permits the use of this efficient printing method for the production of a color-body for the new transfer-sheet or web. The following is an illustrative formula for the preparation of such a varnish or vehicle. Its use involves the use of a hydrocarbon-like toluene, together with an alcohol such as methyl alcohol, as an impregnating solvent for the transfer:

	Parts
50 Chlorinated diphenyl (viscous resinous oil) --	45
Coumarone resin (light colored) -----	15
Castor oil (blown) -----	25
Elemi resin -----	10
55 Elemi oil -----	5

The following is an illustrative formula for the preparation of an ink of non-fixed dye for lithographic printing useful in connection with this process:

	Parts
60 Oil or alcohol sol. dye -----	30
Varnish (as above) -----	70

The finest possible grinding must be effected. Water-soluble dyes cannot be used in this formula. Pigments may be included if it is desirable.

The printing is accomplished in the usual way. Fine detail, screenwork and registration, are perfectly possible. This permits multi-color and continuous tone effects.

The finished printed transfer-sheet or web after a reasonable seasoning of a day or more is ready for use, or may be stored away for later application.

The dyeing, coloring or decorating of absorbent and/or fibrous material, especially leather, by transferring the coloring matter of the new transfer-medium herein disclosed, is preferably accomplished by the use of a hydraulic press, in connection with a previous impregnation of the material to be processed with a suitable solvent or solvent combination, including, if desired, a suitable thickener. But even a heavy calender instead of a hydraulic press can be used for said transferring, especially for material in webs.

The impregnating or samming is done by coating, spraying or swabbing the solvent solution on the front or back or both surfaces of the material to be processed, and leaving this material in a pile, preferably in an air-tight container, for a reasonable time so as to get an even distribution throughout the whole thereof.

The thus impregnated material is then placed on top of a support, preferably a thin metal plate provided with a rubber or felt blanket. The new transfer-sheet or web is then placed on top of the impregnated material, with the color-body lowermost to face the material. To prevent the possibility of smudging, the transfer-medium is preferably held in suspension over said material so as not to touch the same prematurely before the press closes and applies its pressure. No heat or moisture is required. The pressure is variable, an average of 100 pounds per square inch being generally sufficient. The time of pressure application is variable, 20 seconds being generally ample time.

After the application of pressure, the transfer-sheet or web, which sticks slightly to the processed material, is stripped off, leaving its coloring matter entirely or in greater part incorporated or deposited on said material, thereby dyeing, coloring or decorating the same. No water is needed for the removal; the stripping is accomplished by a simple manual pull which separates both materials.

The processed material may thereafter receive an additional solvent spray, especially in the case of plain colors, to provide, if desired, still deeper penetration of the transferred coloring matter into the material.

The coloring matter, by its penetration and by its staining effect, as well as by the capillary attraction, is deeply embedded in the processed material and cannot be removed by ordinary abrasive efforts or with solvents. But, if desired, this condition can be further intensified by spraying or otherwise spreading a suitable coagulating material like albumin, casein, gelatine, or others, over the surface of the processed material and the latter allowed to season. The processed material is then ready for use, or may further be finished in any other usual or desired way.

The foregoing detailed description has, as already pointed out, been based on the assumption that the base material processed is an absorbent and fibrous material like leather. Probably, however, an application of the invention to any absorbent and/or fibrous material, as say cloth or felt, will be substantially as above described. By an absorbent material is meant even a potentially absorbent material, or a material temporarily able to be made abnormally absorbent, as, for instance, celluloid or cellulose acetate. In dyeing, coloring or decorating this material by transfer pursuant to the invention, it is recommended that a fairly light pressure and a solvent or softener for the surface of the base material to

be processed, be used. Such solvent or softener may be methyl ethylene glycol ethyl ether, ethyl lactate or acetone.

The advantages of the new method are many and important, as will have been seen. In regard to leather, particularly, the giving to the same of plain or solid colors has generally been done by vat-dyeing, as presenting the least unsatisfactory of the hitherto known coloration methods. This has involved submerging the hides for a relatively long time in a heated dye-bath. Due to differing porosity characteristics in different hides and in different parts of a hide, to mention one of a number of difficulties encountered, the coloration results have caused considerable rejects and trim-losses, due to lack of uniformity of color or color-shade. The present method, on the contrary, offering to the hide a uniform and concentrated dye-stuff layer as the color-body on a resilient support, and this under high pressure, lays permanently upon the hide a rich and even color of a uniform shade throughout. Not only this, but capillary attraction, pressure and the solvent or solvent mixture preliminarily impregnated in the hide, all combine to cause a relatively deep color penetration. As a result, the color-layer finally in and on the hide is able to withstand any reasonably severe abrasion or stretching without injury to the physical structure of such color-layer or to the general appearance of the finished material. Other and further advantages are present when printed designs constitute the color-body of the transfer-sheet. The rich and variegated color schemes typical of direct liquid-dye printing as used in silk and calico printing may be duplicated on leather and similar materials. Again, photographic reproduction processes can be successfully employed to produce printing plates for depositing the colors to form the color-body of the transfer-sheet, by lithography or otherwise, and panchromatic and half-tone effects are possible. The present application is a continuation in part of application Ser. No. 548,707.

What is claimed is:

1. The process of forming a transfer sheet which comprises the steps of mixing a colloidal bonding protein with a water insoluble colloid of rubber adapted to form a resilient impermeable coating, applying said mixture to a carrier and subsequently evaporating said mixture to form said coating.

2. The process of forming a transfer sheet which comprises the steps of mixing a colloidal bonding protein with rubber, and an emulsifying agent, and applying said mixture in colloidal form to the carrier, said mixture when dry forming a resilient impermeable coating.

3. The process of forming a transfer sheet which comprises the steps of emulsifying a mixture of casein and rubber latex, and subsequently coating a carrier with said emulsion, and air drying said emulsified material and carrier to form a film, said film having a resilient water and alcohol insoluble characteristic.

4. The process of forming a transfer sheet which comprises emulsifying casein and rubber latex, adding to said emulsion formaldehyde and a pulverulent material to reduce tackiness, applying said mixture to a carrier and subsequently evaporating said mixture to form a resilient and dye impermeable coating.

5. The method of preparing a dye transfer sheet for the transfer of decorative markings to absorbent materials which comprises the step of coating a pliable paper carrier with an emulsion composed of a non-water soluble colloid of rubber and a water soluble proteic colloid, a pulverulent filler, formaldehyde, an emulsified fatty substance, an emulsifying agent, and a suitable quantity of water, subsequently drying and coagulating the applied emulsion on the carrier material whereby a bonded layer of insoluble, impermeable, resilient and slightly adhesive coating is formed.

6. A transfer sheet consisting of a carrier, a support thereon, and a color body on said support, said support consisting of a coating having as certain of its ingredients a resilient water insoluble substance composed principally of rubber and a bonding agent, said bonding agent being of the class of proteic colloids including casein, albumin, gelatin and glue, said ingredients forming a film inseparably bonded to said carrier and impermeable to said color body.

7. A transfer sheet consisting of a carrier, a support thereon, and a color body on said support, said support having as certain of its ingredients rubber and a water soluble proteic colloid as a bonding agent, said ingredients forming a film inseparably bonded to said carrier and impermeable to said color body.

8. A transfer sheet consisting of a carrier, a coating thereon, and a color body on said coating, said coating having as certain of its ingredients, a colloid of rubber as a resilient water insoluble substance and a water soluble proteic colloid as a bonding agent, an emulsifying agent and a filler, said ingredients forming a film inseparably bonded to said carrier and being slightly tacky.

9. A transfer sheet consisting of a carrier, a support thereon, and a color body on said support, said support being an evaporated emulsion having as certain of its ingredients rubber, casein, wax and a pulverulent filler, and an emulsified fatty substance, said ingredients forming a film inseparably bonded to said carrier and impermeable to said color body.

10. A dye transfer sheet for the transfer of decorative markings to absorbent materials comprising approximately 40 parts of rubber latex, 10 parts of dry casein, 5 parts of zinc stearate, 5 parts of paraffin emulsion, 2 parts of formaldehyde, 3 parts of triethanolamine and water, said layer being insoluble and impermeable with respect to applied coloring matter and solvents for such coloring matter and completely releasing the coloring matter on application of said solvents, said film being slightly adhesive to prevent the lateral spreading of liquefied dyes during the transfer.

11. A transfer sheet including a carrier, an evaporated emulsion of rubber latex and casein forming a water proof support, and a color body on said support, said color body including a dye-stuff and a resinous non-oxidizing binder.

12. A transfer sheet including a carrier, a water proof support, and a water soluble, multicolor color body on said support, said color body including a dyestuff and a resinous non-oxidizing binder, said binder being thermoplastic.

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