A method for applying a colorant to a cellulosic substrate to improve the resistance of the colorant to removal from the substrate by wetting or rubbing. The method is a two-step process in which the colorant is applied to the substrate in a first step, and in which an elastomeric overcoat is applied to the substrate over the colorant in a second step. The colorant includes a pigment, thickeners and water and can be applied to the substrate in a manner similar to the application of the overcoat, i.e., by any suitable on or off-paper machine process.
METHOD FOR FORMING COLORED CELLULOSIC MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Patent Application Serial No. 60/437,978, which was filed on Jan. 3, 2003.

FIELD OF THE INVENTION

[0002] The present invention relates to dyeing processes, and more specifically to methods for dyeing paper and other cellulosic materials.

BACKGROUND OF THE INVENTION

[0003] On many occasions, it is desired to utilize a cellulosic material product, such as paper, linerboard, paperboard and/or cardboard, that has a specific color for a particular use. For example, when decorating for a special occasion, streamers of various colors are often utilized to provide a festive appearance to the location at which the occasion is being celebrated.

[0004] In order to form products formed of a cellulosic material and having a desired color, many different dyeing techniques have been utilized. While many of these dyeing techniques provided adequate color to the cellulosic material being dyed when finished, a significant problem remained in that the dye often times washed out or bled from the cellulosic material either during the dying process or when the material was contacted by a liquid or simply rubbed against another surface.

[0005] In order to attempt to overcome the bleeding problem, a number of different dyeing compositions and methods were developed. For example, Reinhardt U.S. Pat. No. 4,502,807 discloses a dye stuff that incorporates a thickening mixture including both a synthetic thickening agent and a polysaccharide. The presence of the thickening mixture with these components enhanced the ability of the dye to remain in the proper location on the textile to which the dye was applied. Further, Panto et al. U.S. Pat. No. 4,398,915 discloses a method of preparing bleed resistant colored cellulosics utilizing a colored particle such as a dye/starch complex formed as a reaction product of a starch with a reactive dye compound and a chemical cross-linking agent. Further, Kiesewetter et al. U.S. Pat. No. 5,384,585 discloses the printing of textiles using a dye composition including a reactive dye and a methylcarboxymethyl cellulose as a thickener.

[0006] However, these techniques, while initially providing the paper, linerboard, paperboard or cardboard product with the desired color and an increased level of resistance to bleed or color migration, do not achieve the desired level of resistance to the removal of the colored dye from the product. As a result, colored products are still produced in which the color bleeds from the product, or in which the color can be removed from the product by wetting and/or rubbing a colored surface of the product.

[0007] Therefore, it is desirable to develop a method for dyeing or otherwise coloring a cellulosic product in which the dye or color added to the product is highly resistant to removal from the product.

SUMMARY OF THE INVENTION

[0008] The present invention is an improved method for coloring cellulosic material products in which the color is applied to the product such that the color does not bleed and/or cannot be easily removed from the product. The method or process involves two separate steps which achieve the desired result of applying the color or dye to the product such that the dye is highly resistant to removal.

[0009] The first step in the method involves applying the colorant to the cellulosic substrate in any of a number of well-known application methods. The colorant applied to the cellulosic substrate is formed as an aqueous solution of a thickener, a dye, and water. The thickener can be virtually any suitable material used to thicken and stabilize a dye composition, as will be described. Also, a wide range of dyes can also be used in forming the colorant, as will be described. The colorant formed by the dye, thickener and water can be any suitable colorant used in the printing or dying of cellulosic materials and/or textiles that is able to be applied to the substrate in any of a number of conventional dye application methods and that resists any spreading or migration on the surface of the substrate after application.

[0010] In the second step, an overcoat material is applied to the substrate over the colorant in order to form a protective film over the colorant on the cellulosic material and increase the resistance to removal of the colorant from the substrate. The overcoat material essentially provides a barrier between the colorant and any liquid and/or surface that prevents contact with the colorant, thereby maintaining the colorant on the substrate.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention is an improved method for applying a colorant to a cellulosic substrate in a two-step process which greatly improves the resistance to removal of the colorant on the substrate. While the method is applicable to the application of a colorant or dye to virtually any number of different substrate types, some of the preferred substrates which are capable of being utilized in this method include cellulosic substrates such as white-top linerboard, linerboard, and paper, among others.

[0012] In a particularly preferred embodiment of the method of the invention, the substrate is a white-top linerboard that is defined as a two-ply cellulosic web that has a basis weight of 20 pounds to 90 pounds per 1000 square feet. The base ply is comprised of a virgin material, recycled material, or any combination thereof. The top ply of the cellulosic web is comprised of bleached or de-inked cellulosic fiber with a GE brightness of at least 60.

[0013] Another preferred substrate is linerboard which is defined as a two-ply cellulosic web that has a basis weight of 20 pounds to 90 pounds per 1000 square feet. The base ply is comprised of virgin material, recycled material, or any combination thereof. The top ply of the cellulosic web is comprised of recycled or virgin cellulosic fiber.

[0014] Still another preferred substrate is paper which is defined as a cellulosic web that has a basis weight of 20 pounds to 160 pounds per 3000 square feet. The web may also include filler materials including, but not limited to, clay, calcium carbonate, titanium dioxide, and/or sizing agents.
When applying the colorant to the desired substrate, in the first step, the colorant is added to the substrate in a suitable printing or dyeing process, such as either a conventional off-paper machine application, or an on-paper machine application, including via a size press or water box. Some suitable off-paper machine application processes can include, but are not limited to, flexographic application, rod application, and/or processes utilizing air-knife coaters.

The colorant is most preferably comprised of a solution of a thickener, the pigment, and/or dye stuff, and water in the following proportions:

- 1-30% by weight dye stuff and/or pigment;
- 1-15% by weight a first thickener;
- 1-5% of an optional second thickener (in lieu of or in addition to the first thickener) for rheology modification; and
- the balance, water.

With particular regard to the dye stuff or pigment, the dye stuff for the purposes of this disclosure is defined as any compound within the class of either basic dyes or anionic direct or fiber reactive dyes, or a pigment that can impart a color to a cellulosic material such as a dry coloring matter, usually an insoluble powder to be mixed with water, oil or another base to produce paint in similar products. More particularly, in one aspect of the present invention, there is thus provided a colorant comprising, as a direct dye, a compound represented by the following formula (1):

![Chemical Structure](image)

wherein, ring A represents a benzene ring which may have a substituent or may further be cyclocondensed with another aromatic ring;

B represents an aryl group which may have a substituent or may be coupled with R² to form a heterocyclic structure which will be described later, or a heterocyclic group which may have a substituent or may be coupled with R² to form a heterocyclic structure which will be described later;

D represents a nitrogen atom or a group CR³ (in which R³ represents a hydrogen atom or a C₁₋₅ alkyl group);

E represents a group NR⁵, CR⁶R⁷ or CRⁿCRⁿ⁺₁, in which R⁵ represents a C₁₋₅ alkyl group which may have a substituent, a C₂₋₅ alkenyl group which may have a substituent or an aryl group which may have a substituent, or forms, when taken together with R², a ring which will be described later, and R⁶ and R⁷ each independently represents a hydrogen atom, or a C₁₋₅ alkyl group, an oxygen atom or a sulfur atom;

R¹ represents a C₁₋₅ alkyl group which may have a substituent, a C₂₋₅ alkenyl group which may have a substituent or an aryl group which may have a substituent;
groups, those of the C2-a alkynyl group include ethenyl and propenyl groups, and those of the aryl group include phenyl
d and naphthyl groups, of which the alkyl group is preferred
as R1. Examples of the group which may be a substituent for
them include aryl groups, cyano group, halogen atoms,
hydroxy group, C1-4 alkoxy groups, NR1R2R3 (in which R1R2
and R3 each independently represents a hydrogen atom,
C1 alkyl group, aryl group, alkoxy group, unsubstituted or
monosubstituted aminoC1-a alkyl) group, or (C1-a alkoxy)(C1-a
alkyl)amino group) and a group of the formula (1) from which one hydrogen atom has been
removed.

[0036] Examples of the R2—R3 or R2—R3 in the case where a 5-
to 7-membered nitrogen-containing heterocyclic
structure which may have a substituent is formed by R2
and R3 when they are taken together with N—C—C
at n=0, or by R2 and R3 when taken together with
C—D—N at n=1,
include groups represented by —(CR2R3)n— (in which
R2 and R3 each independently represents a C1-a alkyl
group and m stands for an integer of 2 to 4).

[0037] Examples of the divalent group, as R2, bonded to B
in the case where a 6- or 7-membered heterocyclic structure
which may have a substituent and may have a hetero
atom other than D is formed by bonding of R2 to B when n=0
can include groups —CH=N— and —CO—O—.

[0038] Examples of the anion represented by X− include
chloride ions, bromide ions, iodide ions, trichloroacetic acid
ions, tetrachloroacetic acid ions, sulfonic acid ions,
hydroxylamine ions, methyl sulfonate ions, phosphoric acid ions,
formic acid ions and acetic acid ions.

[0039] The thickener utilized in the formation of the
colorant may be selected from both synthetic and natural
thickeners. More specifically, the composition of the thick-
eners used in the formation of the colorant can vary between
a proportion of 0% for the synthetic thickener and 100% by
weight for the natural thickener, and vice versa, depending
upon the response of the products used to the dyeing of
dye stuffs used. Mixtures which are more preferable regarding
the dispersion stability of the dye stuffs contain between 1 to
30% by weight of the natural thickeners, and most prefer-
bly between 1 to 15%, and 1 to 10% by weight of the
synthetic thickeners, and most preferably between 1 to 5%.  

[0040] The synthetic thickeners are preferably carboxyl
containing synthetic thickenings and the natural thickenings
are based on polysaccharides in preferred embodiments of
the invention. Examples of suitable carbonyl-containing
synthetic thickenings which can be used according to
the invention are aqueous solutions or gel-forming dispersions
of polymerized low molecular weight monoethenically or
polyethenically unsaturated monocarboxylic or dicar-
boxylic acids, such as polyacrylic acid and its homologs, for
example products of polymerizing methacrylic acid or cry-
tonic acid, and polymers of carboxylated derivatives, such as
idaconic or tereconic acid, similarly aqueous solutions of or
dispersions of polymerized maleic acid or its anhydride and
fumaric acid and of its homologs, such as, for example,
citanonid acid or mesaconic acid, further of copolymers of
olefins, for example, ethylene, propylene or butadiene or of
lowelalkylacrylates, optionally substituted acrylamids, vinyl
alcohols, vinyl ethers, vinyl esters, vinyl chloride, vinyl
edene chloride, styrene, acrylonitrile, and analogous alkyl
compounds and the above-mentioned monomers. These
examples also include the reaction products of the polymers
and copolymers described, with polyhydric alcohols and
amines, or amino alcohols, and combinations of highly
polymerized products with less highly polymerized prod-
ucts.

[0041] The polysaccharides used preferably as the natural
thickeners according to the invention embrace optionally
degraded and/or etherified natural products such as high
molecular weight carob bean flour or guar flour and starch
or cellulose ethers. In a particularly preferred embodiment,
the thickener is formed only of material thickeners including
carboxymethyl cellulose and starch.

[0042] While the components of the colorant can be mixed
to form the colorant in any suitable manner, a particularly
preferred method is _____.

[0043] After the colorant has been formed and applied to
the selected surface of the cellulosic substrate, the substrate
may be slightly dried to allow for a limited set of the colorant
on the substrate and to prevent the smearing of the colorant
from the substrate. Further, the colorant application rate can
vary depending upon the color shade depth desired on the
surface of the substrate. For example, in a preferred embodi-
ment the application rate of the colorant is 140% by weight
of the substrate and more preferably 1.1-15% by weight of
the substrate.

[0044] After the application of the colorant to the sub-
strate, in the second step of the method, a film of a suitable
overcoat material is applied as an overcoat to the colored
cellulosic substrate to impart the requisite wet and dry rub
fastness for the colorant reacted onto the substrate. The
application methods for the overcoat material are similar to
printing or dyeing methods used for the application of
the colorant and can include, but are not limited to, off-paper
machine application methods, such as flexographic, roll,
and/or knife air coaters. Further, with regard to the overcoat
material the material is a natural or synthetic rubber formed
from various compounds, including but not limited to poly-
butadiene, polyisobutylene, polysyrene, polyacrylates and
polyurethanes. In a preferred embodiment the material is a
latex, which for the purposes of this invention is defined as
any material within the class of modified styrene butadiene-
based polymers or modified styrene acrylate polymers with
provisions for changes in polymer TG value or polymer
combination. More preferably, the overcoat may be a 50%
solids latex product which is used as a “varnish” layer over
the substrate, to provide wet and dry rub fastness and to add
gloss or matte finish to the substrate. Further, the overcoat
application rate to the substrate can vary depending upon
the level of fastness and the gloss level required for the
substrate, with greater fastness properties and higher gloss
achieved with a higher overcoat application rate. More
specifically, in a preferred embodiment the application rate
for the overcoat will be within a range of 1% to 25% by
weight of the substrate and more preferably between 1% and
5% by weight of the substrate.

[0045] Colored linerboard produced as described may be
used in any corrugated application, e.g. point of purchase
displays or corrugated containers. Application of the over-
coat material enhances printability of the material and
ensures that the print medial does not bleed into the under-
lying dyed substrate.
[0046] Various alternatives are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter regarded as the invention.

We hereby claim:

1. A method for coloring a substrate, the method comprising the steps of:
   a) providing a cellulosic substrate;
   b) applying a colorant to the substrate, the colorant including a pigment, a thickener and a solvent; and
   c) applying an overcoat to the substrate over the colorant.

2. The method of claim 1 wherein the substrate is selected from the group consisting of:
   white-top linerboard, linerboard and paper.

3. The method of claim 1 wherein the pigment is selected from the group consisting of a basic fiber reactive dye, an anionic fiber reactive dye, and dry coloring matter.

4. The method of claim 1 wherein the thickener is present in an amount of between 1% and 40% by weight.

5. The method of claim 4 wherein the thickener is selected from the group consisting of: natural thickeners, synthetic thickeners and combinations thereof.

6. The method of claim 5 wherein the natural thickeners are polysaccharides.

7. The method of claim 5 wherein the natural thickener is selected from the group consisting of starch, carboxymethylcellulose and combinations thereof.

8. The method of claim 7 comprising:
   a) starch in an amount of between about 1% and 25% by weight of the colorant; and
   b) carboxymethyl cellulose in an amount of between about 0% and 10% by weight of the colorant.

9. The method of claim 9 wherein the pigment is present in an amount of between about 1% and 50% by weight of the colorant.

10. The method of claim 9 wherein the pigment is present in an amount of between about 1% and 30% by weight of the colorant.

11. The method of claim 1 wherein the step of applying the colorant comprises dispensing the colorant at an application rate of between about 1% to 40% by weight of the substrate.

12. The method of claim 1 wherein the overcoat is an elastomer.

13. The method of claim 12 wherein the overcoat is selected from the group consisting of polybutadienes, polyisobutyltetnes, polystyrenes, polyacrylates, and polyurethanes.

14. The method of claim 12 wherein the overcoat is a latex.

15. The method of claim 12 wherein the step of applying the overcoat comprises dispensing the overcoat at an application rate of between about 1% and 25% by weight of the substrate.

16. The method of claim 1 wherein the step of applying the colorant is performed in a process selected from the group consisting of off-paper machine applications or on-paper machine applications.

17. The method of claim 1 wherein the step of applying the overcoat is performed in a process selected from the group consisting of off-paper machine applications or on-paper machine applications.

18. A colored substrate formed by a process comprising the steps of:
   a) providing a cellulosic substrate;
   b) applying a colorant to the substrate, the colorant including a pigment, at least one thickener selected from the group consisting of synthetic thickeners, natural thickeners and combinations thereof, and water; and
   c) applying an overcoat to the substrate over the colorant, wherein the overcoat is an elastomer.

19. A colored cellulosic substrate comprising:
   a) a sheet of a cellulosic substrate;
   b) a colorant applied to a surface of the substrate, the colorant including a pigment, at least one thickener selected from the group consisting of synthetic thickeners, natural thickeners and combinations thereof, and water; and
   c) an overcoat applied to the surface over the colorant, wherein the overcoat is an elastomer.

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