

[54] **METHOD OF FORMING PATTERNS ON
SUBSTRATE SURFACES**

[72] Inventor: **Fred E. Long**, Stow, Ohio
[73] Assignee: **The General Tire & Rubber Company**
[22] Filed: **Aug. 18, 1969**
[21] Appl. No.: **851,039**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 758,145, Sept. 6, 1968, abandoned.
[52] U.S. CL. **117/45, 117/37, 117/41, 117/138.8 R, 117/138.8 B**
[51] Int. Cl. **B44d 1/16, B44d 5/06**
[58] Field of Search **117/37, 41, 45, 138.8 R, 138.8 B, 117/138.8 A**

[56] **References Cited**
UNITED STATES PATENTS

2,326,001	8/1943	Adriotti	117/37
2,467,228	3/1949	Pritzker	117/45
2,467,229	3/1949	Pritzker	117/45
2,612,456	9/1952	Thacker et al.	117/41
3,202,527	8/1965	Stevens	117/45

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—M. F. Esposito
Attorney—Frank C. Rote, Jr. and Denbigh S. Matthews

[57] **ABSTRACT**

This invention concerns a process of forming an aesthetically pleasing random pattern on the surface of a substrate comprising the steps of coating the surface with a retractable liquid, the retractable liquid having a surface tension that is at least about 2 dynes/centimeter above the critical surface tension of wetting of the surface and also concerns the articles produced by this process.

10 Claims, No Drawings

METHOD OF FORMING PATTERNS ON SUBSTRATE SURFACES

This application is a continuation-in-part of application Ser. No. 758,145, filed Sept. 6, 1968 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the field of coatings. More specifically, this invention relates to the field of decorative coatings and to a process of forming a random pattern coating on a surface.

2. Description of the Prior Art

A fundamental principle in obtaining commercial success is to fashion one's commodity to appeal to the purchaser's aesthetic senses. In regard to industrial equipment, such a practice comprehends using compact design, mute colors, and smooth finishes. In respect of more consumer related articles such as items of wear, household furniture, etc., this practice involves the use of aesthetically appealing colorful patterns on the surface of these items. It has been proven time and time again that between two or more competing items of equal quality and utility, the article that is the most aesthetically appealing is the more commercially successful.

There are many conventional methods of making and applying colorful patterns to surfaces such as off-set printing, hand painting, stenciling, and silk screening. This invention concerns a new and novel method of making and applying colorful patterns to relatively smooth surfaces. It makes available to the designer and decorator another useful tool.

Basically, this invention comprises a process of making reproducible random patterns on surfaces. In addition to providing for an aesthetically appealing pattern that is easy to apply and that may be easily varied, the process of this invention is relatively inexpensive and may be used on virtually any substrate.

Therefore, the main object of this invention is a new and useful process of producing an aesthetically desirable, colorful pattern on a surface of a substrate. Other objects of this invention include a process that is easy and inexpensive to undertake, that provides for virtually an infinite variety of random patterns each of which is reproducible, a process that may be applied to virtually any substrate, a process that utilizes most, if not all, existing dyes and pigments, and a process in which some of the components may be recovered for reuse so as to make the process even more commercially attractive, and a process that is amenable to automatic and semi-automatic control.

SUMMARY OF THE INVENTION

This invention concerns a process of forming a random pattern on a surface comprising coating the surface with a retractable liquid, the retractable liquid having a surface tension of at least about 2 dynes/centimeter above the critical surface tension of wetting of the surface and concerns the articles produced by this process.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In its most rudimentary form, the process of this invention comprises coating a surface with a retractable liquid. The liquid coating retracts into an aesthetically pleasing random pattern almost immediately. In addition, the dried pattern may be protected by top coating or may be used as is.

This novel process utilizes the physics of "wetting." Surface wetting is a phenomena based on the surface tension of the liquid and the critical surface tension of wetting of the surface. The scientific aspects of this phenomena are known in the art, see for example, "Textbook of Physical Chemistry," by Glassstone, Second Edition, D. Van Nostrand Company Inc. See also, "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution," by W. A. Zisman, published in "Contact Angle—Wettability and Adhesion," Advances in Chemistry, Series 43, American Chemical Society, Washington, D. C., 1964, pages 1-51.

Basically, these texts disclose that each surface has a property known as a critical tension of wetting (CST); liquid it has been described in terms of interfacial tensions, contact angles, and various mathematical equations none of which are specifically required to understand or undertake the practice of this invention. Liquids having a surface tension higher than this critical surface tension of wetting will not wet the surface but will bead up into small bubbles of liquid. An example of this phenomenon is the familiar appearance of rain on the surface of a newly waxed automobile; the rain water retracts into little beads or globules. Conversely, when the surface tension of the coating liquid is lower than the critical surface tension of wetting, the surface will be wet by the liquid. An example of this phenomenon is the appearance of the same automobile after being scrubbed with a strong solution of detergent; the surface is covered by a relatively even layer of liquid.

When a liquid does not wet the surface, it retracts to form many small droplets of liquid that are interspersed on areas of non-wetted (i.e., dry) surface—hence, the term "retractable" liquid. These droplets are better termed "globules" to eliminate the inference that they are purely spherical; these globules may be spherical but in most cases will take the form of odd shaped, e.g., pyramidal, mounds of liquid. In other situations such as with more viscous retractable liquids, the retracted pattern may take the form of "fish eyes" or circular areas of non-wetted surface interspersed on a coating of the liquid. This particular phenomenon will be described more fully later.

For a liquid to be "retractable" its surface tension should be at least about 2 dynes/centimeter greater than or above the critical surface tension of wetting of the surface to which it is applied. At a surface tension between the CST of the surface and about 2 dynes/centimeter above this value, the retracted pattern may still form, however, the driving force of retractability (difference in the two surface tensions) is so small that the pattern may highlight local imperfections or discontinuities either in the surface or in the coating liquid. As the aforesaid scientific texts indicate, there is an upper practical difference in driving force of retractability of these retractable liquids at about 40 dynes/centimeter. That is to say, in comparing the surface tensions of most liquids with the critical surface tensions of wetting of most surfaces, the maximum difference is about 40 dynes/centimeter. This is not to say, however, that the retractable liquid may not have a surface tension of more than 40 dynes/centimeter above the critical surface tension of wetting of the surface; it merely indicates that 40 dynes/centimeter is about the practical limit.

The basic pattern effects of this invention are made by coating a substrate surface with a retractable liquid and then causing the globules that form thereon to take on a different color than the background.

An example of this process, in its simplest form, is coating a surface with a retractable liquid comprising a colorant and a vehicle for the colorant. The retractable liquid will form into globules of color-containing vehicle and, thereafter, the dried pattern will consist of colored areas, formed from the globules, interspersed among a background of the original surface color. More sophisticated patterns may be produced by refinements in this process and these will be more fully described later.

For the purpose of this discussion, the term "colorant" will be used herein to denote matter whose primary function is to impart a color or colors to whatever it is applied to. The term "colorant" includes dyes, pigments, and other color-lending compounds. Also for the purpose of this discussion, the terms dye and pigment are used to denote colorants that are soluble and insoluble, respectively, in a vehicle. Included in the term "pigment" are powdered metals that lend sparkle as well as color to the patterns. Finally, the term "vehicle" is used herein to denote a liquid media in which the colorants are carried, either in solution in the case of dyes, in dispersion in the case of pigments, or both. Vehicles include solvents, non-solvents, and mixtures of different liquids.

In general, there are few limitations on the overall process of this invention. One such limit is the requirement that the surface tension of the retractable liquid be higher or greater than the critical surface tension of wetting of the surface by at least about 2 dynes/centimeter. If it were lower, the coating would either not retract and therefore form a continuous film over the surface or retract poorly, showing minor surface or liquid irregularities as described earlier. Another limit is that the coating must not be applied so thick as to prevent retraction into the pattern. Generally, this limit is rather difficult to exceed, however, when dealing with viscous retractable liquids there is the possibility that the coating may be applied too thick (e.g., flooding) to allow retraction into a random pattern. Conversely, the coating should not be applied so thin as to prevent a random pattern from forming. This would occur where the vehicle is, for example, a volatile solvent and the coating applied so thin that the vehicle evaporates before the coating has had time to retract into a pattern.

The retractable liquid is generally comprised of a vehicle, colorants, and other optionally added materials such as thickeners and surfactants.

The vehicles operable in this invention include water, organic solvents, solvent systems such as water and miscible organic solvents, and others. The primary requirements of the vehicle are to carry the colorants for deposition on the surface and to have a surface tension great enough to permit compounding with colorants and other materials, into a retractable liquid, and yet retain its surface tension above the critical surface tension of wetting of the surface to be coated. A limitation on the vehicle is that it should not be one that chemically reacts with the surface or the substrate or physically reacts therewith with any more than possibly slightly solubilizing the substrate; this latter aspect will be discussed later. As will be more fully explained later, different types of vehicles make different types of random patterns. Generally speaking, water does not affect the background of the surface whereas organic solvents do affect the background and, in addition, organic solvents may provide an anchoring function to the pattern.

In Table I are listed a number of vehicles along with their observed surface tensions. It should be noted that the surface tensions of all liquids are generally dependent upon purity and absence or presence of other additives. The surface tensions listed for the vehicles in Table I represent general products of commercial (not pharmaceutical) purity but without any known additives.

TABLE I

Vehicle	Surface Tension dynes/cm
Chlorobenzene	27.0
P-Xylene	28.5
Benzene	29.5
Styrene	32.2
Ethylene dichloride	33.2
Pyridine	37.1
Acetophenone	38.8
Benzyl Alcohol	40.2
Aniline	42.2
Tributyl phosphate	28.2
Diethyl phthalate	30.4
Diethyl sebacate	31.5
Water	73.1
Dimethyl formamide	36.9
Tetrahydrofuran	33.5

In addition to those vehicles listed above, other vehicles include hexane, ethyl butyrate, ethyl acetate, n-octanol, toluene, dimethyl acetone, dioxane, diethyl formamide, dimethyl sulphate liquid monomers, formic acid, cyclopentanone, dimethylsulfoxide and quinoline.

Some materials can be used as a plasticizer in conjunction with a certain type of substrate in one system and as a vehicle in another system.

The process of this invention may be applied to virtually any substrate. The primary requirement for the substrate is that its critical surface tension of wetting be either less or modifiable to less than the surface tension of the retractable liquid applied thereto. The substrates over which this process may be utilized include plastics, metals, glass, and liquids. Another general requirement of the substrate is that its surface be relatively smooth so as not to adversely affect the retractability of the retractable liquid.

Because the critical surface tension of wetting is a function of only the surface, the bulk of the substrate may be ignored and attention focused on the top two or three atomic layers. This means that even though certain substrates might not be amenable to having a pattern formed thereon, because of adverse critical surface tension of wetting, inability to anchor the coatings, etc., this process may still be utilized thereon by first coating the surface thereof with a finite layer of a material that remedies the defect such as by having a critical surface tension of wetting less than that of the retractable liquid or by permitting good anchoring of the subsequently applied pattern to the substrate (this latter feature is known as a "tie-coat" in coating parlance). For instance, it is theorized that steel has a very high CST so that most liquids would wet the surface and not produce a retracted pattern. By first coating the steel surface with say polyethylene (CST=31.0) the surface would have a CST of 31.0, well within the range of most vehicles to form a pattern thereon.

Table II below is a list of substrates along with their critical surface tensions of wetting for their smooth surfaces. By comparing the CST's of these substrates in Table II to the surface tensions of the vehicles in Table I, one may get a general indication of those vehicles that will make a retractable liquid for certain substrates. It should be kept in mind, however, that most additives will reduce the surface tension of the vehicle to which they are added so that care must be exercised not be "overload" a vehicle and stifle the retractableness of the pattern-forming liquid. If high loadings (of colorants, etc.) are contemplated, one should consider choosing a vehicle with a higher initial surface tension.

TABLE II

Substrate	CST dynes centimeter
Polyvinyl chloride	39.0
Polyvinylidene chloride	40.0
Polyethylene terephthalate	43.0
Polyhexamethylene adipate	46.0
Polymethyl methacrylate	39.0
Polyvinyl alcohol	37.0
Polystyrene	33.0
Polyethylene	31.0
Polyvinylfluoride	28.0
Polytetrafluoroethylene	18.5

The method of applying the coating of retractable liquid to the surface of the substrate is not critical to the operability of this invention provided, however, that the coating be uniform and of constant thickness throughout. Virtually any conventional method of coating will suffice for this process such as wiping, doctor blade application, draw bar use, and so on. As disclosed earlier, the method should neither be such as to permit the retractable liquid to flood the substrate and prevent retraction nor be applied so thin as not to permit the pattern to form.

The random patterns produced by this process may be changed by varying a number of different conditions, however, this process will reproduce the same random patterns if the conditions from one run are preserved identical in another

run. Methods of changing the random patterns formed by the process of this invention include changing dyes, changing or including pigments, utilizing different vehicles, altering the viscosity of the retractable liquid, changing the surface tension of the retractable liquid, altering the thickness of the deposit of the coating, and changing the critical surface tension of wetting of the surface.

The use of dyes in the process of this invention produces many aesthetically beautiful patterns. Virtually any dye is usable herein, such as dyes of the nitroso, nitro, mono-azo, diazo, trisazo, tetrazo, stilbene, pyrazolone, ketonimine, di- and triphenylmethane, xanthene, acridine, quinoline, thiazole, indamine, indophenol, azine, aniline black, oxazine, thiazine, sulfide, hydroxyketone, anthraquinone acid and mordant, anthraquinone vat, aryldio quinone vat, and indigoid families. Generally, dyes are merely referred to by their color even though their molecular makeup may vary from compound to compound. By placing a dye in the retractable liquid and utilizing the process of this invention, the random pattern that is formed generally contains the dye concentrated in the liquid globules while being absent from the non-wetted areas of the surface from which the liquid retracted. Therefore, the dried random pattern consists of dry-colored, dried globule areas interspersed on the background color of the substrate. The aforesaid situation occurs in the case of a water vehicle and organic solvent vehicles that do not swell or enter into partial solution with the substrate to which they are applied. Where, however, the vehicle swells or partially solubilizes the substrate, the pattern is changed to that of the dye covering all of the surface lightly while being more concentrated, and thusly darker, in the dried areas of the globules.

The use of pigments in the process of this invention produces many startling effects. Virtually any pigment may be used herein both inorganic and organic, such as iron oxide reds, toluidine reds, chrome yellows, orthonitraniline orange, chrome oxide greens, and many, many others. These insoluble pigments, dispersed in the retractable liquid, remain in the liquid phase (i.e., the globules) when the pattern is formed. Thereafter, they are under the combined affects of gravity, inter-molecular dipole influences with the globule, and the vehicle surface tension. Many of the pigments migrate to the outer reaches of the globule-surface interface and form rings around the globules much like a sand beach about the perimeter of an island. If more than one pigment is used, their different migration rates cause them to form successive rings about the dried area once occupied by the globule. The use of powdered metal pigments, such as aluminum powder, copper powder, gold powder, and silver powder produces beautiful pattern effects such as sparkling.

It can readily be seen that the number and variety of patterns produced by combinations and subcombinations of these materials will produce virtually a limitless variety of surface patterns.

The choice of vehicle greatly influences the type of pattern produced by this process. Vehicles that do not swell, partially solubilize, or enter into the molecular structure of the surface generally carry the colorants only into the globules and do not permit them to color the non-wetted areas of the surface. For example, in the case of a retracting liquid, comprising water as the vehicle, a water soluble dye, and a dispersed pigment, being coated on the surface of a piece of polyvinyl chloride plastic, the water carries the dye and pigment almost entirely into the globules leaving the non-wetted PVC surface virtually unaffected and uncolored.

Vehicles that swell, partially solubilize, or otherwise enter into the molecular structure of the surface affect the patterns in a number of ways. First, the dyes color all of the surface, both wetted portions and non-wetted portions, during the initial stages of the coating step. The dyes and pigments continue, however, to concentrate in the globules after retraction so that the patterns take on a light-dark color scheme. Secondly, these types of vehicles permit the pattern to become more firmly anchored in the surface and provide a more wear

resistant pattern. For example, in the case of a retracting liquid, comprising dimethyl sulfoxide as a vehicle, a dye, and a pigment, being coated on the surface of a piece of polyvinyl chloride plastic, the vehicle partially solubilizes the plastic and permits the dye to lightly color the entire surface of the polyvinyl chloride prior to the liquid retracting into a pattern. After retraction, the dye and pigment are concentrated in the globules of liquid. After drying, it is readily apparent that the pattern is strongly anchored to the surface of the plastic—it does not smear when rubbed with the finger; the preceding pattern (utilizing water as a vehicle) smears rather easily.

Startling pattern effects are achieved by using vehicles comprised of two or more liquids such as a mixture of organic solvents or a mixture of water with various miscible organic solvents. Mixtures of solvents permit one to achieve the added benefit of good pattern anchoring, by using swellable solvents such as dimethyl sulfoxide, benzyl alcohol, and pyridine in the case of polyvinyl chloride plastic surfaces, and to utilize a wider range of dyes that are soluble in only a limited number of solvents. Using mixtures of miscible organic solvents with water as vehicles permits one to achieve pattern anchoring, different background effects, and the use of water soluble dyes.

Regardless of the anchoring aspect of organic solvent vehicles, one may additionally choose to place a top coat (clear or colored) over the dried pattern for other purposes such as to enhance the luster, wear resistance, and abrasion resistance of the pattern. An example of top coats that provides these features are commercially available clear urethane polymers.

It is rather obvious that the patterns are to be dried to render the surface handleable. The step of drying these patterns may be accomplished in most any conventional manner provided care is taken to maintain the drying conditions such that the substrate is not harmed such as by being melted or charred.

This drying step may also be conducted under conditions whereby the vehicle is recaptured for later reuse (recycle). These methods, known in the art, are such as the use of absorbent columns, liquefaction, etc. Use of such a drying method makes this process more commercially attractive.

Another method of changing the pattern effects in the process of this invention is to alter the viscosity of the retractable liquid. Generally, increasing the viscosity of the liquid will make the pattern more coarse, i.e., increase the size of and spacing between the globules. At a high enough viscosity, depending upon the system used, the coating will cease to retract into globules and instead form a continuous film having small "fish eyes" or round dry spots dispersed throughout the films. Such patterns as these are not particularly aesthetically appealing. In addition, it should be noted that increasing or altering the viscosity of the retractable liquid will produce a change in the surface tension thereof and care must be taken to insure that the surface tension is not decreased below the critical surface tension of wetting of the surface. Methods of thickening or changing the viscosity of the coating liquid include, in the case of a water vehicle system, adding a thickener such as polyvinyl alcohol or cellulose derivatives. In the case of organic solvents, there are commercially available thickeners to perform the same function.

Another method of altering the patterns produced by the process of this invention is to change the surface tension of the retractable liquid. Generally, the closer the surface tension of the liquid is to the critical surface tension of wetting of the surface, the finer the pattern, i.e., the smaller the size of the globules. By increasing the surface tension of the liquid, or separating it further from the CST of the surface, a coarser or larger globule pattern is produced. In cases where the surface tension is lowered, it has been noted that there is produced an additional pattern effect called "spider webbing"; this effect takes the form of thin, thread-like trails of liquid between the globules that cut across the unwetted surface.

A still further method of changing or altering the patterns produced by the process of this invention is to change the

thickness of the coating of liquid initially deposited on the surface. Generally, as the coating is increased in thickness the pattern will be coarser, i.e., the globules will be larger. Conversely, as the coating is made thinner, the pattern will be finer, i.e., the globules will be smaller. As described earlier, care must be taken to insure that the coating is not so thick as to prevent the retracting of the liquid nor should the coating be so thin as to allow the vehicle to evaporate prior to the coating retracting to form the pattern.

A still further method of changing the patterns is by changing the critical surface tension of wetting of the surface. Generally, increasing the critical surface tension of wetting of the surface has the same effect as lowering the surface tension of the retractable liquid, i.e., the surface tension of the liquid and the CST of the surface are drawn closer together; in this situation a finer pattern is produced. Conversely, decreasing the critical surface tension of wetting of the surface has the same effect as increasing the surface tension of the retractable liquid, i.e., the surface tension of the liquid and the CST of the surface are driven further apart; in this situation a coarser pattern is produced. The critical surface tension of wetting of a surface may be changed simply by placing a finite coating of a liquid or other material on the surface of the substrate. In the case of metal substrates, such as in steel beams, such could be made by placing a finite coating of paint or plastic on the surface thereof.

Particularly in the area of plastics, it has been shown both theoretically and practically, that plasticized plastics have a critical surface tension of wetting substantially equal to the surface tension of the plasticizer used therein when the

pattern forming process, the efficacy of the process as described herein, the effect of varying certain factors in the process, the ease with which the process is performed, and the wide range of materials usable therein. These examples are given to aid those skilled in the art as to the practice of this invention and are not to be construed, either singly or in combination, as placing a limitation thereon as the invention is defined by the claims that follow the examples. All percentages listed hereinafter are percentages by weight and all parts are parts by weight per 100 parts plastic unless otherwise noted. Also, the patterns produced by the process of this invention are aesthetically appealing and do not provide any function other than decoration so that they are not capable of physical measurement. Thus, the changes in the patterns are purely of subjective characterization and will be described as such leaving to those who desire to practice this process the enjoyment of visualizing the fruits of their own labor.

EXAMPLE 1

A series was prepared of retractable liquids, each containing 1 percent orange pigment and 1 percent blue dye, in different vehicles and the surface tensions of each were measured. Quantities of these liquids were coated onto a number of different smooth substrate surfaces by pouring a quantity of the liquid onto one end of the substrate specimen and drawing a wire-wound draw bar across the liquid and substrate surface to spread the liquid into a coating. Below in Table 1 are listed these substrates and liquids along with their critical surface tensions of wetting and surface tensions, respectively, and an indication as to whether a retracted random pattern formed thereon.

TABLE 1

Substrate surface	Measured surface CST dynes centimeter	Retractable liquid vehicle	Retractable liquid measured surface tension dynes centimeter	Presence of pattern
Polyvinyl chloride containing 40 parts dioctyl sebacate.....	28.4	Dimethyl formamide....	34.8	Yes.
Do.....	28.4	Dimethyl sulfoxide.....	33.3	Yes.
Polyvinyl chloride containing 40 parts tricresyl phosphate.....	36.3	Ethyl acetate.....	22.4	No.
Polyvinyl chloride containing 40 parts dioctyl phthalate.....	28.4	Toluene.....	26.7	No.

plasticizer is present in amounts greater than about 15 parts by weight per 100 parts plastic. In addition, it has been shown that the top two or three atomic layers of plasticized plastics is virtually pure plasticizer. Therefore, in plastics, such as for example plasticized polyvinyl chloride, the critical surface tension of wetting is substantially equal to the surface tension of the plasticizers used therein. This holds true for most of the plasticizers used in plastics such as phosphate types like cresyl diphenyl phosphate and tricresyl phosphate, phthalate types like dioctyl phthalate, dibutyl phthalate, and dimethyl phthalate, sebacate types like dioctyl sebacate and dibenzyl sebacate, adipate types like di-2-ethylhexyl adipate and di-isodecyl adipate, epoxy types like epoxidized soybean oil and iso-octyl epoxy stearate, and the polymeric types like glyceryl mono-recinoleate and glyceryl mono-oleate. Generally, these plasticizers are in amounts varying from about 10 parts (by weight) to 50 parts per 100 parts of plastic, however, the CST of the plasticized plastic surface becomes substantially equal to the surface tension of the plasticizer only when the plasticizer is above about 15 parts (by weight) per 100 parts of plastic. Below that amount, the CST of the plastic is generally at or near to the surface tension of the plastic per se.

Following are examples that demonstrate the theory of the

This example shows that the pattern-forming ability of the retractable liquid occurs when the surface tension of the retractable liquid is above or greater than the critical surface tension of wetting of the surface to which it is applied and does not occur when the surface tension of the retractable liquid is less than the CST of the surface. It should also be noted that the term "retractable liquid" is somewhat of a misnomer when used in connection with a surface that has a CST greater than the surface tension of the liquid because the liquid will not retract when applied thereto. This apparent discrepancy is, however, not of sufficient magnitude to create any confusion in the minds of those who are skilled in the art.

EXAMPLE 2

A series was prepared of retractable liquids, each containing 1 percent orange pigment and 1 percent blue dye, in different vehicles and the surface tensions of each were measured. These liquids were applied to different substrates in a fashion identical to that described in Example 1. Below in Table 2 are listed these substrates and liquids along with their critical surface tensions of wetting and surface tensions, respectively, and an indication as to whether a retractable random pattern formed thereon.

TABLE 2

Substrate surface	Measured surface CST dynes centimeter	Retractable liquid vehicle	Retractable liquid measured surface tension dynes centimeter	Presence of pattern
Polyvinyl chloride containing 40 parts tricresyl phosphate.....	36.3	Dimethyl sulfoxide.....	39.7	Yes.
Polyvinyl chloride containing 40 parts dioctyl phthalate.....	28.4	Dioctyl phthalate.....	29.6	No.
Polyvinyl chloride containing 40 parts dioctyl phthalate.....	28.4	Styrene.....	29.4	Yes.

This example shows that the random pattern, produced by the process of this invention, is not consistently produced when the surface tension of the retractable liquid is less than about 2 dynes/centimeter above or greater than the critical surface tension of wetting of the surface. Also, this example shows that the surface tension of a bare liquid (dioctyl phthalate) has a surface tension of 30.4 dynes/centimeter—see Table 1) is lowered by the addition of foreign materials; here, the 1 percent blue dye and 1 percent orange pigment lowered the surface tension to 29.6 dynes/centimeter.

EXAMPLE 3

A series was prepared of retractable liquids, each containing pigments and dyes, in different vehicles and applied to different substrates in a fashion identical to that described in Example 1. Below in Table 3 are listed these substrates and liquids along with their critical surface tensions of wetting and surface tensions, respectively, the colorants incorporated therein, and an indication as to whether a retractable random pattern formed thereon.

TABLE 3

Substrate surface	Measured surface CST dynes/centimeter	Retractable liquid additives	Retractable liquid additives	Retractable liquid measured surface tension dynes/centimeter	Presence of pattern
Polytetrafluoroethylene.....	20.1	1% orange pigment, 1% blue dye.....	Dimethyl formamide.....	34.8	Yes.
Do.....	20.1	do.....	Dimethyl sulfoxide.....	39.3	Yes.
Do.....	20.1	do.....	Ethyl acetate.....	22.4	Yes.
Do.....	20.1	do.....	Toluene.....	26.7	Yes.
Polyvinyl chloride containing 40 parts dioctyl phthalate.....	28.4	do.....	Styrene.....	29.4	Yes.
Do.....	28.4	do.....	Dimethyl aniline.....	29.4	Yes.
Polytetrafluoroethylene.....	20.1	do.....	Dioctyl phthalate.....	29.6	Yes.
Polyvinyl chloride containing 40 parts dioctyl phthalate.....	28.4	do.....	Dimethyl sulphate.....	37.9	Yes.
Do.....	28.4	do.....	Quinoline.....	42.6	Yes.
Do.....	28.4	do.....	Dioxane.....	32.1	Yes.
Do.....	28.4	1% blue dye.....	Water.....	70.0	Yes.
Do.....	28.4	0.4% red dye.....	do.....	70.0	Yes.
Do.....	28.4	1% blue dye.....	1:1, Water/dimethylformamide.....	53.4	Yes.

This example demonstrates the wide range of vehicles that may be used in the process of this invention and further shows that they include organic solvents, water, and water/miscible organic solvent mixtures.

EXAMPLE 4

A series was prepared of retractable liquids, each containing 1 percent blue dye, in a water vehicle to which was added a compound that affected the viscosity of the liquid, viz. a commercial water-soluble hydroxy ethyl cellulose resin, and applied to different substrates in a fashion identical to that described in Example 1. Below in Table 4 are listed these sub-

strates and liquids along with their critical surface tensions of wetting and surface tensions, respectively, the viscosities of the liquids, an indication as to whether a retractable random pattern formed thereon, and if a pattern did form, a subjective indication as to its coarseness.

This example shows that the degree of coarseness of the random pattern, formed by the process of this invention, may be controlled by varying the viscosity of the retractable liquid.

EXAMPLE 5

A series was prepared of retractable liquids in different vehicles each containing 1 percent blue dye; different types of blue dyes were used so that it was soluble in whatever vehicle was used. These liquids were applied in two ways to a substrate surface of polyvinyl chloride plastic containing 50 parts of dioctyl phthalate plasticizer. First, the liquid was applied in a fashion identical to that described in Example 1 and then wiped from the substrate after 30 seconds to determine the percentage of coating liquid picked up (by polymer swelling,

45

partial solubilization of the substrate, etc.) by the substrate. Secondly, the liquid was applied to another set of similar substrates in a fashion identical to that described in Example 1 and the dried pattern observed as to the extent of coloration of the surface. These liquids are listed below in Table 5 along with the percentage of vehicle pickup by the polyvinyl chloride and subjective observations as to the degree of coloration in the pattern.

50

This example shows that the coloration of the non-wetted areas of the surface over which the retractable liquid is initially coated (prior to retraction of the liquid) may be controlled by varying the ability of the vehicle to be picked up by the surface substrate.

55

60

TABLE 4

Substrate surface	Measured surface CST dynes/centimeter	Retractable liquid additives	Retractable liquid measured surface tensions dynes/centimeters	Retractable liquid measured viscosity, cps.	Presence of pattern	Coarseness of pattern
Polytetrafluoroethylene.....	20.1	1% blue dye.....	70.0	1	Yes.....	Very coarse.
Do.....	20.1	1% blue dye, 7% resin thickener.....	38.8	308	Yes.....	Coarse.
Do.....	20.1	1% blue dye, 12.5% resin thickener.....	33.0	6,150	Yes.....	Medium.

TABLE 5

Vehicle	Percent of vehicle picked up by PVC in 30 seconds	Pattern coloration
Water.....	0	Sharp, no coloration of non-wetted areas.
Formamide.....	0	Do.
Dimethyl sulfoxide.....	3.2	Sharp, medium coloration of non-wetted areas.
Benzyl alcohol.....	0.46	Sharp, light coloration of non-wetted areas.
Pyridine.....	20.4	Fuzzy, dark coloration of non-wetted areas.
1:10 benzyl alcohol/pyridine.....	20.0	Do.
1:5 benzyl alcohol/pyridine.....	15.0	Do.
1:1 benzyl alcohol/pyridine.....	10.0	Fuzzy, medium coloration of non-wetted areas.
5:1 benzyl alcohol/pyridine.....	5.0	Well defined, medium coloration of non-wetted areas.
10:1 benzyl alcohol/pyridine.....	2.4	Sharp, light coloration of non-wetted areas.

EXAMPLE 6

A series was prepared of retractable liquids in different vehicles, each containing 1 percent blue dye, and applied to the surface of substrates of polyvinyl chloride containing different amounts of dioctyl phthalate plasticizer in a fashion identical to that described in Example 1. Table 6 below lists the vehicles and their surface tensions, the amounts of plasticizer utilized in each substrate along with their critical surface tensions of wetting, and an indication as to whether a retracted pattern formed thereon.

TABLE 6

Vehicle—benzene

Retractable liquid measured surface tension—28.5 dynes/centimeter

Parts Plasticizer	Measured Surface CST dynes /centimeter	Presence Of Pattern
0	42	No
5	38	No
10	35	No
20	30	No
30	30	No
40	30	No
50	30	No
80	30	No

Vehicle—styrene

Retractable liquid measured surface tension—32.0 dynes/centimeter

Parts Plasticizer	Measured Surface CST dynes /centimeter	Presence Of Pattern
0	42	No
5	38	No
10	35	No
20	30	Yes
30	30	Yes
40	30	Yes
50	30	Yes
80	30	Yes

Vehicle—ethylene dichloride

Retractable liquid measured surface tension—32.5 dynes/centimeter

Parts Plasticizer	Measured Surface CST dynes /centimeter	Presence Of Pattern
0	42	No
5	38	Ill defined
10	35	Ill defined
20	30	Yes
30	30	Yes
40	30	Yes
50	30	Yes
80	30	Yes

This example shows that when a plasticizer is incorporated into the plastic substrate the critical surface tension of wetting of the substrate surface becomes substantially that of the plasticizer after a level of about 15 parts plasticizer has been

achieved. This example also demonstrates the ability of the process to be used to produce a random pattern on substrates that initially do not have SCT's sufficiently low enough to permit pattern formation by the step of incorporating additives that alter the CST of the surface to a value that will permit this process to be used.

EXAMPLE 7

A retractable liquid was prepared using aniline as the vehicle and including 1 percent blue dye and 5 percent aluminum powder; this liquid had a measured surface tension of 40.0 dynes/centimeter. A polyvinyl chloride plastic surface was separated into areas and the surface of each area wiped with a different material. The retractable liquid was then applied to these surface areas in a fashion identical to that described in Example 1. Table 7 below lists these wiped materials and their measured critical surface tensions of wetting along with an indication as to whether a random pattern formed thereon.

TABLE 7

Wiped Material	Measured Surface CST Dynes /Centimeter	Presence Of Pattern
Nothing	42	No
Dioctyl phthalate	30	Yes
Dioctyl sebacate	31	Yes
Tributyl phosphate	28	Yes

This example shows that, in addition to incorporating materials into the substrate to reduce the surface's CST to a level that will permit use of this process as demonstrated in Example 6, the CST of the surface may be altered to permit this process by merely applying a coating, of a material that has a surface tension (if a liquid) or a critical surface tension of wetting (if a solid) lower than the surface tension of the retractable liquid, to the substrate surface prior to applying the coating of the retractable liquid.

What is claimed is:

1. A process of preparing an aesthetically pleasing article consisting of applying a thin coating of a retractable liquid to a noncoated surface, said retractable liquid comprising a colorant and a vehicle, said vehicle consisting of a liquid having a surface tension of at least about 2 dynes/centimeter greater than the critical surface tension of wetting of said surface so that said liquid will retract into a random pattern of less total area than said surface, and drying said random pattern coating.
2. The process of claim 1 including the subsequent step of applying a thin, uniform coating of a film-forming top coat over said dried pattern.
3. The process of claim 1 wherein said vehicle is selected from the group consisting of water, organic solvents, organic solvent mixtures, and water/water-miscible organic solvent mixtures and wherein said colorant is selected from the group consisting of dyes, pigments and mixtures thereof.
4. The process of claim 1 wherein said retractable liquid contains a thickener.
5. The process of claim 1 wherein said retractable liquid includes powdered metals.
6. The process of claim 1 wherein said vehicle swells said

13

surface during said coating step to more firmly anchor said dried random pattern coating thereto.

7. The process of claim 1 wherein said surface comprises a plastic.

8. The process of claim 7 wherein said plastic is plasticized.

9. An article comprising at least one nonporous, substantially smooth surface having an aesthetically pleasing decorative pattern thereon, said pattern formed by a process consisting of applying directly thereto a thin coating of a retractable

14

liquid, said retractable liquid comprising a colorant and a vehicle, said vehicle consisting of a liquid having a surface tension of at least about 2 dynes/centimeter greater than the critical surface tension of wetting of said surface so that said liquid will retract into a random pattern of less total area than said surface, and drying said random pattern coating.

10. The article of claim 9 including a uniform top coat film over said dried pattern coating.

* * * * *

10

15

20

25

30

35

40

45

50

55

60

65

70

75