**Title**: DIFFERENTIAL GLOSS PRODUCTS AND METHODS OF MAKING THE SAME

A method of making a differential gloss product which comprises: forming a gelled, potentially foambale, base resinous material (12); printing thereon a predetermined pattern (14), some portions containing a urethane polymerization catalyst and either the same or other portions containing a foaming inhibitor; applying to the printed pattern a resinous wear layer (16); gelling the resinous wear layer and foaming and fusing the resinous materials; applying a urethane top coating composition (18) containing no urethane polymerization catalyst to the resinous wear layer; heating to polymerize the portions of the urethane coating composition (18B) lying directly over the portions containing the urethane polymerization catalyst (14B) to create interspersed high gloss polymerized surfaces; mechanically embossing the entire urethane coating to cause texturing of the entire surface, applying a urethane polymerization catalyst substantially uniformly to the entire surface of said urethane coating composition either before or after the mechanically embossing step; and heating the thus textured urethane coating and said catalyst to polymerize the remaining surfaces of the urethane coating composition (18) to create thereat low gloss surfaces due to the mechanical embossing whereas the portions of the urethane coating which had been polymerized previously revert back to their original high gloss appearance.
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DIFFERENTIAL GLOSS PRODUCTS AND METHODS
OF MAKING THE SAME

THE FIELD OF THE INVENTION

The present invention relates to decorative sheet materials, and more particularly to multi-layered, resinous, decorative sheet materials having surface portions having differential gloss effects, and to methods of making such differential gloss, decorative sheet materials. Even more particularly, the present invention relates to differential gloss, decorative sheet materials having raised, embossed or textured surface areas in substantially perfect registry with the surface areas having the surface differential gloss effects. Such decorative sheet materials having differential gloss
are of use as: floor, wall or ceiling coverings; desk, table or counter tops; and a host of other commercial, industrial and household applications.

THE GENERAL BACKGROUND OF THE INVENTION

Decorative sheet materials of a resinous polymer composition have been made for many years and one of the commonest ways of creating or enhancing the surface decorative effects has been to provide selected portions of the surface of such decorative sheet materials with different types of contrasting finishes or effects, or surface gloss or luster differentials, for example, with smooth, glossy or lustrous surfaces; raised, embossed dead or dull mat surfaces, raised, embossed glossy or lustrous surfaces; smooth, dead or dull mat surfaces; etc., all sharply contrasting with one another to create differential gloss products.

Many methods, including differential mechanical embossing, inlaying, or chemical embossing or etching, and many other methods, have been devised to provide sharply contrasting surface areas but all of such prior art methods or combinations thereof have always left something to be desired. For example, differential mechanical embossing procedures combined with pattern or design printing procedures has always created registration problems and related difficulties. Inlaying procedures and chemical etching methods have normally been more costly and more process-time consuming.

In U. S. Patent 4,187,131 there is disclosed a process for producing a surface covering having both dull areas and glossy areas. This differential gloss effect is accomplished by printing a decoration in the surface of a
base with some printing composition containing a free-
radical polymerization catalyst, e.g. a peroxide, applying
a wear layer, e.g. polyvinyl chloride, which includes a
polymerizable monomer having at least two ethylenically
unsaturated groups which are polymerizable by the peroxide,
over the printed surface, gelling the coating, mechanically
embossing the gelled surface, and then heating to fuse the
composition and polymerize the portion of the monomer in
contact with the peroxide. The result is the direct retention
of the mechanical embossing in the areas where the monomer
has been polymerized and its loss where polyvinyl chloride
had been fused. The resulting product has dull surface areas
corresponding to where the peroxide was applied and gloss
areas in the other portions of the surface.

In U. S. Patent 4,298,646, issued to the same
inventors as herein, and assigned to the same assignee,
there is described a related invention in which the entire
surface of the urethane coating is given a dusting of a
powdered particulate or granular material containing a
urethane polymerization catalyst, and the excess of said
material is removed from the polymerized, high gloss areas,
prior to heating to polymerize the remaining unpolymerized
surfaces of the urethane coating thereby to create low gloss
surfaces thereat due to the continued presence of the
occluded particles or granular materials therein.

PURPOSES AND OBJECTS OF THE INVENTION

It is therefore a principal purpose and object
of the present invention to provide resinous polymer
compositions in sheet material form having selective, surface
decorative effects created by the controlled placement of
various different surface finishes, raised embossings, or
surface gloss differentials, wherein smooth or embossed, glossy or lustrous surface areas sharply contrast with each other and with smooth or raised embossed dead or dull matte finish surfaces, using methods in which registration errors, problems and difficulties are substantially completely eliminated and which methods are neither costly nor process-time consuming.

BRIEF SUMMARY OF THE INVENTION

It has been found that such principal purposes and objects, and other principal purposes and objects which will become clear from a further reading and understanding of this disclosure, may be accomplished by providing a method of making a differential gloss product which comprises: forming a potentially foamable base resinous plastisol on a supporting structure, such as a fibrous backing sheet, heating and gelling the potentially foamable base resinous plastisol; applying to the surface of the gelled plastisol a printing ink composition in a predetermined pattern or design, some portions of which contain a urethane polymerization catalyst and either the same or other portions of which contain a blowing or foaming inhibitor; applying to the surface of the printed, gelled base resinous plastisol a resinous plastisol wear layer; heating and gelling the resinous plastisol wear layer and blowing or foaming the potentially foamable base resinous plastisol at elevated temperatures and fusing the base resinous plastisol and the resinous wear layer; applying to the surface of the fused resinous wear layer a urethane coating composition containing no urethane polymerization catalyst; applying heat to
polymerize the urethane coating composition to those surface portions lying directly over the printing ink portions containing urethane polymerization catalyst, whereby such polymerized surface portions of the urethane coating composition are given a relatively high gloss and a relatively hard surface, whereas the unpolymerized surface portions of the urethane coating composition remain tacky and fluid or semi-fluid; mechanically embossing the entire urethane coating to cause texturing of the unpolymerized, tacky areas; applying to the entire surface of the interspersedly polymerized urethane coating composition either before or after the mechanically embossing step a urethane polymerization catalyst; and applying heat to polymerize those tacky, fluid or semi-fluid surface portions of the urethane coating composition which had not been previously polymerized but which now are polymerized but now are given a relatively lower or reduced gloss surface due to the mechanical embossing thereof whereas the portions of the urethane coating which had been polymerized previously revert back to their original high gloss appearance.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following specification and accompanying self-explanatory drawings, there are described and illustrated preferred and typical embodiments of the present invention but it is to be appreciated that the present invention is not to be construed as limited to such preferred and typical embodiments as are specifically disclosed and illustrated therein but to include other similar and equivalent embodiments, as are determined by the scope and the spirit of the appended claims.
Referring to the accompanying self-explanatory drawings,

FIGURE I is a fragmentary, diagrammatic, elevational, cross-sectional view of one embodiment of the present invention, subsequent to the heating and fusing of the resinous materials, plus blowing or foaming if a blowing or foaming agent was originally included in the base resinous plastisol material composition and if a blowing or foaming inhibitor was originally included in some portions of the printing ink composition; and

FIGURE II is a fragmentary, diagrammatic, elevational, cross-sectional view of another embodiment of the present invention under process conditions similar to those of Figure I. As will be described in greater detail hereinafter, Figure II may represent a different product than that illustrated in Figure I or it may represent a different portion of the product illustrated in Figure I.

These Figures have not been drawn precisely or accurately to scale. Some portions and some dimensions have been drawn to a slightly larger scale, whereas certain other portions and other dimensions therein have been drawn to a slightly smaller scale. This has been done merely to bring out more clearly some of the details of the smaller portions and elements and to accentuate some of the more important features and aspects of the present invention, such as the thickness of the printing ink composition layer which has been increased manyfold in the Figures for a clearer understanding of its various portions.
GENERAL DESCRIPTION OF THE INVENTION

The present invention will be generally described and illustrated primarily with reference to Figure I which is a preferred and typical embodiment of the invention but which is not to be construed as limitative of the broader aspects of the inventive concept. In Figure I, there is illustrated a relatively flat, fibrous backing sheet material 10 upon which is deposited or formed a conventional, potentially foamable, base resinous plastisol composition 12, or, if desired or required, a conventional, non-foamable, base resinous plastisol composition which does not contain any blowing or foaming agent.

THE BACKING SHEET MATERIAL

A relatively flat, backing web or sheet material 10 may be used, if desired or required, as the base layer or supporting substrate for the base resinous polymer compositions of the present inventive concept. Such a backing sheet material 10 may comprise a felted or matted fibrous sheet of overlapping, intermingled fibers and/or filaments; or a nonwoven, knitted, woven, or otherwise fabricated textile construction; or a sheet of resinous polymer composition; or paper or a paper product; or similar or like materials and constructions. A felted fibrous sheet material comprising inorganic fibers, such as asbestos; or organic fibres, such as cellulose, cotton, jute or rayon; or synthetic or manmade fibers and/or filaments, such as polyolefins, polyamides, acrylics, polyesters, glass, etc., are the most commonly used backing sheet materials but others are equally suitable and are utilizable in special situations. Such backing sheet materials are well set forth in many prior art patents, such as United States Patents 3,293,094,
3,293,108, 3,660,187 and 4,187,131. The thickness of such a relatively flat, fibrous backing sheet material 10 will depend to a large extent upon the particular product to be made and the particular subsequent use for which it is intended. Normally, such a thickness is in the range of from about 10 mils to about 90 mils, but other thicknesses, especially those greater than 90 mils, may be used in particular and special circumstances.

THE BASE RESINOUS POLYMER COMPOSITION

The relatively flat, backing sheet material 10 may be omitted completely and the foamble or non-foamble resinous polymer composition 12 may be used by itself. such resinous polymer composition 12 may be made by well-known standard and conventional methods and may contain one or more synthetic resins, such as a polymer or co-polymer of vinyl chloride, or other resins such as polyurethane, an elastomer such as natural or synthetic rubber, and the like, as the main constituent resin.

Other constituents of such resinous polymer compositions 12 include: a blowing or foaming agent, such as azodicarbonamide, if a blowing or foaming agent is desired or required; various accelerator/stabilizers or catalysts such as dibasic lead phthalate, zinc octoate, lead octoate, dibasic lead phosphite, etc.; various light and/or heat stabilizers, such as metallic soaps; one or more plasticizers such as dioctyl phthalate, butyl benzyl phthalate, dibutyl sebacate, etc.; coloring agents and pigments such as titanium dioxide; solvents and diluents such as methyl ethyl ketone, mineral spirits, etc.; fillers such as clay and limestone; and many other conventional and well-known additives and improvement agents.
Although a polymer or co-polymer of vinyl chloride in the form of a plastisol is the preferred and typical synthetic resin to be incorporated into the base resinous polymer composition, many other resins are of equal applicability, not only in plastisol form but also in organosol, latex or solvent form. The specific resin and its particular form of use as it is being utilized does not relate to the essence of the inventive concept and many other resins are set forth in the previously mentioned United States Patent.

If no backing sheet material, such as a felted or matted fibrous web, is to be used, then the base resinous composition may be doctoried by a doctor blade, or roll coated, or poured, or cast, or otherwise applied or formed on a strippable supporting carrier which may be a steel belt, a rubber belt, release paper, or felt or other fabric or material having a release surface or coating thereon and subsequently stripped or removed therefrom.

However, if a backing sheet material 10 is to be used and is to remain as part of the final product, then the base resinous composition 12 may be doctoried by a doctor blade, or roll coated, or poured, or cast, or otherwise applied or formed and adhered to the carrying sheet material, such as the fibrous backing sheet material 10, in a substantially uniform manner in a relatively uniform thin coating by procedures well-known in the art. The thickness of such a base resinous composition 12 as a foamable material, as applied and still wet, is in the range of from 5 mils to about 50 mils, or even more, if so desired or required by its subsequent use.
THE GELLING OF THE BASE RESINOUS COMPOSITION

After the base resinous plastisol composition 12 has been applied or formed on the carrying backing sheet material, it is then heated under moderately gentle heat for a period of time of from about \( \frac{1}{2} \) minute to about 4 minutes at an elevated temperature of from about 240°F. to about 400°F., but more normally commercially from about 290°F. to about 350°F., whereby the plastisol gels and firms so that it can be more easily handled and processed in subsequent operations. The elevated temperature, however, is not that sufficiently high as to activate or to decompose the particular blowing or foaming agent which may be present as to cause blowing or foaming of the base resinous polymer composition.

THE PRINTING OF THE GELLED BASE RESINOUS COMPOSITION

The gelled, firm base resinous composition 12 is then cooled and is printed or coated with a suitable printing ink composition or compositions 14 in the desired or required pattern or design which may possess many colors. The particular pattern or design which is used does not relate to the essence of the invention and any suitable pattern or design may be selected. The printing procedure, in general, is conventional and should require no further description, inasmuch as such procedures are well known in the industry and are described in many publications and patents.

THE BLOWING OR FOAMING INHIBITORS

If it is desired that different levels or heights of the blowing or foaming effects be obtained, then, pre-determined portions or parts 14A of the particular pattern
or design printed on the surface of the base resinous polymer compositions 12 contain a blow modifier or inhibitor in different amounts, concentrations, or types, and so forth, depending upon the variety of differential blowing or foaming effects desired. Such differential blowing effects are well described in the previously mentioned United States Patents and should need no further explanation or description.

Such blowing or foaming inhibitors are normally included in the particular printing ink composition in amount of from about 1% to about 35% by weight, based on the total weight of the printing ink composition. Many typical blowing and foaming inhibitors are mentioned in the previously described United States Patents, among the more popular are:

- trimellitic anhydride
- fumaric acid
- benzotriazole

Naturally, if no blowing or foaming effects or chemical embossing effects are desired as a result of subsequent heating procedures, then, no blow modifying agents or inhibitors are included in the printing ink composition 14 and the heights and levels and the extent of the blowing or foaming operation is substantially uniform. Some typical and well known conventional printing ink compositions are noted in the previously mentioned United States Patents.

THE URETHANE POLYMERIZATION CATALYSTS

Also, as shown in Figure I, in predetermined parts or portions 14B of the predetermined pattern or design, which parts or portions 14B are shown in different places of the predetermined pattern or design in Figure I,
but which may be the same places and, as a matter of fact, there may even be places where is neither blowing or foaming inhibitor nor urethane polymerization catalyst, there is included a urethane polymerization catalyst in an amount of from about ½% to about 20% by weight, based on the total weight of the printing ink composition in which it is included. Preferred and typical examples of such urethane polymerization catalysts are:

dibutyl tin dilaurate
dibutyl tin di-2-ethylhexanoate
dibutyl tin diacetate
dibutyl tin maleate
dibutyl tin oxide
tetramethyl tin
dimethyl dioctyl tin
stannous octoate
lead octoate
zinc octoate
zinc 2-ethylhexanoate
lead naphthenate
copper naphthenate
diethyl cyclohexylamine
N-methyl morpholine
N,N-dimethyl ethanolamine
N-methyl diethanolamine

In some instances, as required or desired by existing conditions and circumstances, a relatively small amount, say, from about ½% to about 2% by weight, a low concentration, of the urethane polymerization catalyst may also be included in the portions or parts 14A, in order to
modify, adjust, or control the relative degree of
tackiness of the superjacent surfaces of the wear layer
lying directly thereover, such as in the surface areas 18A.

THE RESINOUS WEAR LAYER

The printed, gelled potentially foamable base
resinous polymer composition 12 is then allowed to dry
and a resinous wear layer 16 in the form of a resinous
polymer composition or plastisol is then applied thereto
substantially uniformly. Such a wear layer 16 contains
conventional and standard constituents, such as synthetic
resins, preferred and typical being polymers or co-
polymers of vinyl chloride, medium to low molecular weight,
and plasticizers, stabilizers, pigments or dyes on rare
occasions, solvents and diluents, viscosity improvement
and controlling agents, and like additives and materials.
The concentrations of such added constituents are
conventional and standard and are in the ranges and
concentrations set forth in the previously mentioned
United States Patents.

The relatively flat, resinous wear layer 16
has an average thickness of from about 0.002 inch to
about 0.025 inch and is applied substantially uniformly
to the surface of the printed, gelled and firmed base
resinous polymer composition 12. The wear layer 16, in
normal practice, is usually a clear, unpigmented resinous
polymer composition and its basic purpose in usually to
give to the final product improved wearing properties
and qualities.
THE GELLING OF THE RESINOUS WEAR LAYER

After the wear layer 16 has been applied to the printed, gelled base resinous composition 12, it may be desired to gel and firm its surface in a separate operation. If it is, then the wear layer is heated under moderately gentle heat in an oven or other heating device for a period of from about ½ minute to about 4 minutes at an elevated temperature of from about 240°F. to about 400°F., whereby it hardens or firms and gels so that it can be handled more easily in subsequent operations. Again, the elevated temperatures must not be that high as to activate or to decompose the blowing or foaming agent which is normally present in the base resinous composition 12, if blowing or foaming is desired in the final product but not desired at this particular time in the manufacturing process.

However, if it is desired that blowing and foaming, as well as fusion of the resinous materials, take place in the same procedure at elevated temperature along with the gelling of the wear layer, such may be easily accomplished by heating in an oven or other suitable heating device to an elevated temperature which is higher than the previously stated temperatures for gelling. Such more elevated temperatures are in the range of from about 325°F. to about 470°F. for a period of time of from about 1 minute to about 4 minutes. Such heating procedures are standard and conventional and are described in the previously cited United States Patents.
THE URETHANE TOP COATING COMPOSITION

A urethane top coating composition 18 is then applied or formed substantially uniformly on the blown or foamed and fused surface of the resinous wear layer 16 to a depth or thickness of from about 0.0005 inch to about 0.015 inch. The specific and particular urethane top coating composition 18 which is employed does not relate to the essence of the present invention and normally comprises a substantially uniform mixture of unreacted polyols or polyhydroxy compounds and unreacted polyisocyanates, as originally applied to the surface of the resinous wear layer 16, along with additives, such as surfactants, or other constituents, as desired or required. However, such a top coating urethane coating composition 18 does not contain any urethane polymerization catalysts or any urethane polymerization initiators. As a consequence, the polyols and the polyisocyanates do not react with each other to any substantial degree at the time of the application to the blown or foamed and fused resinous wear layer.

The polyols or polyhydroxy compounds may be selected from a very wide range of suitable diols, triols, tetrols, or various other polyols and polyhydroxy compounds, or mixtures thereof, from many various sources, including glycols, polyether glycols, polyester glycols, glycerols, trialkylol alkanes, alkane triols, polyether triols, polyester triols, erythritol, pentaerythritol, polyols having a functionality higher than four, caprolactone polyols poly (hydroxyalkyl) derivatives of such compounds as the alkylene polyamines, the various polyether polyols with amines, etc. One example of the latter-most groups is
N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine. Mixtures of polyols may be used.

The polyisocyanates may be selected from a large group of aliphatic, aromatic, cycloaliphatic, and heterocyclic polyisocyanates, such as methylene-bis (4-cyclohexylisocyanate), isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl-isocyanate), 2,4,4-trimethyl-hexamethylene diisocyanate, etc. Mixtures of polyisocyanates may be used.

THE CURING OF THE URETHANE TOP COATING COMPOSITION

The blown or foamed and fused resinous material with the applied urethane top coating composition 18 thereon is then exposed to elevated temperatures of from about 250°F. to about 425°F. and preferably from about 270°F. to about 420°F. for a period of time of from about 2 minutes to about 10 minutes in an oven or other suitable heating means, whereupon the polymerization reaction between the polyols and the polyisocyanates in the urethane top coating composition 18 is initiated. However, such polymerization reaction is initiated only in those portions or parts 18B of the urethane top coating composition 18 which lie directly over the predetermined parts or portions 14B of the printing ink composition 14 containing the urethane polymerization catalyst. During such heating procedure, such urethane polymerization catalyst has apparently migrated from the printing ink composition areas 14B to polymerize the areas 18B of the urethane top coating composition 18 to a hardened, cured high glossy condition. However, the other parts or portions 18A of the urethane top coating composition 18 which do not lie directly over any catalyst-containing area are substantially uncured and remain tacky and fluid or semi-fluid and remain in a very soft state, as contrasted to the
parts or portions 18B of the urethane top coating composition 18 which are cured and polymerized to a firm, hardened, glossy or shiny condition which is substantially tack-free.

THE MECHANICAL EMBossING PROCEDURE

In the following description of the mechanical embossing procedure, emphasis will be placed on the obtaining of a flat, dead or dull matte finish or texture which is roughened, corrugated, contoured, knurled, lined or the like. Such may be obtained by means of proper pressure dies or similar tools, or by pressing the surface of the wear layer against a roughened or desirably corrugated or contoured surface, such as a fibrous paper surface, an uneven or roughened metallic surface, a fabric, or any coarse, grainy surface which is not smooth, sleek, glossy or lustrous, preferably with a material that has release characteristics, such as silicone rubber.

The depth of the mechanical embossing may be as little as a fraction of a mil or it may be as much as about 15 mils, but preferably is from about 1 mil to about 4 mils, depending upon the type, thickness, and the nature of the wear layer being so embossed mechanically upon the decorative effect which is desired or required, upon the type and the form of the mechanical embossing, and so forth.

At the conclusion of the mechanical embossing procedure, the unpolymerized areas, tacky or slightly tacky, become embossed. The cured areas remain glossy. Such a finish or texture is substantially completely lacking in brilliance, gloss, luster or sheen. The surface may be roughened, corrugated, coarse, lined or knurled in regular
or irregular, predetermined or random fashion and may possess numerous very small knobs, projections, ridges, points, or protuberances to give it the desired flat, dead or dull matte appearance. The mechanical embossing may also take the form of very many, very fine lines which are straight and parallel or swirling curves, as many as about 60 or 80 or even 100 or more lines per inch, or it may be the result of pressing paper, textured materials or fabrics, woven, knitted or nonwoven against the surface of the wear layer to create thereon the desired finish or texture. The embossing material preferably has release characteristics, such as silicone rubber.

The mechanical embossing to yield the desired flat, dead or dull matte finish or texture or other finishes may take place under pressures which may be as low as about 2 pounds per square inch gauge up to about 300 pounds per square inch gauge, depending upon the existing temperature which is in the range of from about 240°F. to about 470°F. If the pressure is applied in a press platen, the pressure may be maintained for a period of time of from about 10 seconds to as much as about 4 minutes. If the pressure is applied by means of a heated embossing roll, then the temperatures and the pressures will be in the higher portions of the aforementioned ranges, whereas the time of the application of the pressure will be correspondingly relatively short. However, the passing or the wrapping of the resinous polymer sheet material around a portion of the periphery of the heated embossing roll can be used to extend the duration of the application of heat. The pressures which are exerted, however, must be sufficient as to establish a good intimate contact between the heated embossing surface and the resinous polymeric materials.
being embossed.

With further reference to the development of the sleek, glossy, or lustrous finish, as compared to the retention of the flat, dead or dull finish, the following numerical comparative gloss levels and ranges should exist for the satisfactory application of the principles of the present inventive concept.

The sleek, glossy or lustrous finish areas should have gloss levels in the range of from about 15 to about 90, or even higher; the flat, dead or dull mat finish areas should have gloss levels in the range of from about 70 down to about 3, or even less; with the differences in the gloss levels between the two contrasting finishes being in the range of at least about 10 in gloss level ranges below 50 and at least about 20 in gloss level ranges equal to or about 50. Such numerical gloss level values are determined by the procedures set forth in A.S.T.M. 523-67 (1972) at an angle of 60°.

It is also to be observed that reference to sleek, glossy or lustrous finishes, as compared to flat, dead or dull mat finishes, is merely a typical or preferred embodiment of the present inventive concept. These terms or phrases are comparative or relative terms or phrases and are used merely or primarily to indicate differences in gloss levels.

For example, the principles of the present inventive concept are equally applicable to the obtaining of a sleek, glossy or lustrous finish in some certain selected areas and the obtaining of even more sleek, glossy or lustrous finishes in certain other selected areas, again keeping the differences in the gloss level values greater than about 20, inasmuch as the gloss level values greater than about 20, inasmuch as the gloss levels involved in such embodiment will be greater than about 50.
The final resulting product, in one form thereof, greatly resembles a ceramic tile flooring such as in commonly found in bathrooms, both as floor and as wall surfaces. The sleek, glossy or lustrous finish greatly resembles the surface of a glazed or fired ceramic tile, whereas the flat, dead or dull matte surface greatly resembles the grout or cementitious materials which are placed between the glazed ceramic tile.

THE APPLICATION OF A SECOND AMOUNT OF URETHANE POLYMERIZATION CATALYST

An additional amount of urethane polymerization catalyst then is applied to the surface of the mechanically embossed product. The catalyst can be applied by any manner such as by spraying it on the surface or passing the sheet through a coating operation. Alternatively, the catalyst in dry powder form can be dusted on the surface of the product. Alternatively, the urethane polymerization catalyst can be applied to the entire surface of the urethane top coating before the mechanical embossing step. This sequence actually can improve the retention of the embossing pattern and the release of the embossing medium from the urethane coating. If desired, a release agent may be incorporated into the catalyst composition.

THE SECOND CURING OPERATION

The multi-layered resinous construction with the additional layer of urethane polymerization catalyst thereon is then exposed to elevated temperatures of from about 250°F. to about 425°F. and preferably from about 270°F. to about 420°F. for a period of time of from about 2 minutes to about 10 minutes in an oven or other suitable heating means, whereupon the polymerization reaction between the
polyols and the polyisocyanates in the urethane top coating areas 18A is initiated. Apparently, the urethane polymerization catalyst has migrated thereinto and has initiated such a polymerization reaction. This time, however, the portions or the parts 18A, although they harden and cure, do not achieve a high gloss or shiny appearance, due to the mechanical embossing which have created a roughened, somewhat pebbled surface having a very irregular surface texture, in sharp contrast to the smooth shiny, high gloss surface areas 18B.

It is noted that the roughened surface of the mechanical embossing is retained after polymerization in areas 18A whereas, in contrast thereto, the previously polymerized portions 18B, which had been temporarily roughened by the mechanical embossing, revert back to their original high gloss condition. It is also to be observed that the smooth, shiny, high gloss surface areas 18B are in substantially perfect registry with the catalyst-containing portions 14B of the printing ink composition and that the roughened, pebbled, dead, dull surface areas 18A are in substantially perfect registry with the inhibitor-containing portions 14A of the printing ink composition, as well as with the relatively raised, chemically embossed surface areas and the relatively depressed, chemically embossed surface areas of the resinous wear layer, as well as the urethane top coating.

The resinous urethane top coating composition 20 is substantially completely cured or polymerized in all surface areas, that is, 18A and 18B, as a result of the two curing operations and is thus substantially monomer free.
THE EMBODIMENT OF FIGURE II

The embodiment of Figure II illustrates an application of the basic principles of the present invention in a slightly different manner in order to achieve a slightly different differential gloss effect, on a slightly different final product.

In Figure II, corresponding structural elements and constituents have been given the same reference numbers as their counterparts of Figure I with the sole difference being the addition of a superscript (') in order to clearly identify the relationship between the various products. In Figure II, a potentially foamable (or non-foamable) base resinous polymer composition 12' is applied or formed as a substantially uniform layer on the surface of a typical fibrous backing sheet material 10'. The gelling operation to firm the surface of the applied base resinous polymer composition 12' is identical to that previously described with reference to Figure I.

A printing ink composition 14' is then applied to the surface of the gelled, firmd potentially foamable base resinous polymer composition 12' but, in this embodiment, both a blowing or foaming inhibitor and a urethane polymerization catalyst are included in the same parts or portions 14A' of the printing ink composition 14', whereas the parts or portions 14B' contain neither the blowing or foaming inhibitor nor the urethane polymerization catalyst.

In some instances, again, as required or desired by existing conditions and circumstances, a relatively small amount or low concentration of the urethane polymerization catalyst may also be included in the parts or portions 14B' in order to modify, adjust, or control the degree of tack of the superjacent portions lying directly thereover, such as in the surfaces of the urethane top
coating composition 18B', to be described hereinafter.

The printed, gelled potentially foamable base
resinous polymer composition 12' is then allowed to dry
and a resinous wear layer plastisol composition 16' is
substantially uniformly applied or formed thereon in the
same fashion as previously described with reference to
Figure 1. Gelling of the applied resinous wear layer
plastisol composition 16' to firm its surface takes place
as previously described. Blowing or foaming and fusion
may take place simultaneously or successively with the
gelling operation.

It is to be noted that, as a result of the
blowing or foaming and fusion procedure, the areas of the
resinous wear layer 16' which lie directly over the
portions of the printing ink composition 14' containing
both the blowing or foaming inhibitor and the urethane
polymerization catalyst, that is, portions 14A', are in a
normal unembossed, relatively lower condition, whereas
the other portions of the resinous wear layer 14' which
do not lie over the portions 14A' are in a raised or expanded,
relatively higher condition. Such expansion or chemical
embossing is essentially opposite to that described for
Figure 1 and illustrated therein.

In such an application of the principles of
the present invention, care should be taken to insure the
complete compatibility of the blowing or foaming inhibitor
and the urethane polymerization catalyst which are both
in the portion 14A' of the printing ink composition 14'
so that there is no appreciable or significant reaction
or interaction between the two components of that particular
printing ink composition.
A urethane top coating composition 18' is then applied or formed substantially uniformly on the surface of the blown or foamed and fused multi-layered product and contains a substantially uniform mixture of unreacted polyols and unreacted polyisocyanates, additives such as surfactants and other agents, but again there is no inclusion of any urethane polymerization catalysts. The polyols and polyisocyanates are as previously described herein. The thickness of the applied layer of urethane top coating composition 18' is again in the range of from about 0.005 inch to about 0.015 inch, although greater or lesser thickness may be employed for special conditions and circumstances.

The curing of certain surfaces portions 18A' of the applied urethane top coating composition 18' proceeds at an elevated temperature under the previously described blowing or foaming and fusion temperatures. As a result, the surface portions 18A' of the applied urethane top coating composition 18' are polymerized and cured to a hardened, shiny and glossy condition, whereas the surface portions 18B' which do not lie directly over a urethane polymerization catalyst portion 14A' remain relatively soft, fluid or semi-fluid, unpolymerized and uncured.

The mechanical embossing procedure is repeated as in Embodiment I and a urethane polymerization catalyst as previously in connection with the embodiment of Figure I is then dusted on or otherwise applied to the entire surface of the urethane top coating composition 18' to form a substantially uniform layer thereon.

Such multi-layered product is then exposed to the elevated temperatures of the second curing operation, as described previously, whereby the portions 18B' of the urethane top coating composition 18' are also cured or polymerized.
As a result, the resinous urethane top coating composition 18' is substantially completely cured or polymerized in all surface areas 18A' and 18B' and is substantially completely monomer free. Such result is generally comparable to the results obtained in the embodiment of Figure I, although in sort of a reverse fashion.

The raised, chemically embossed surface areas 18B' are dead and dull, have a pebbly, roughened appearance and a relatively low gloss effect. The relatively lower, chemically unembossed surface areas 18A' are shiny and glossy and create an excellent contrast to the dead and dull areas 18B'. It is also to be observed that there is substantially perfect registry with the corresponding portions 14A' and 14B' of the pattern or design of the printing ink composition 14'.

Consideration of the Figures indicates that there are four possible major basic variations of the differential gloss effects products of the present invention, as follows:

(1) When the particular printing ink composition applied to a particular part or portion of the surface of the base resinous polymer composition contains both a blowing or foaming inhibitor and a urethane polymerization catalyst, such as noted in areas 14A' of Figure II, the corresponding portion of the surface of the urethane top coating composition lying directly thereover will have a normal chemically unembossed height and will have a shiny, smooth, high gloss surface, such as noted in areas 18A'.
(2) When the particular printing ink composition applied to a particular part or portion of the surface of the base resinous polymer composition contains only a blowing or foaming inhibitor and no urethane polymerization catalyst, such as noted in areas 14A of Figure I, the corresponding portion of the surface of the urethane top coating composition lying directly thereover will have a normal chemically unembossed height and will have a dull, dead, low gloss surface, such as noted in areas 18A.

(3) When the particular printing ink composition applied to a particular part or portion of the surface of the base resinous polymer composition contains only a urethane polymerization catalyst and no blowing or foaming inhibitor, such as noted in areas 14B of Figure I, the corresponding portion of the surface of the urethane top coating composition lying directly thereover will have a raised or expanded chemically embossed height and will have a smooth, shiny, high gloss effect, such as noted in areas 18B.

(4) When the particular printing ink composition applied to a particular part or portion of the surface of the base resinous polymer composition contains neither a blowing or foaming inhibitor nor a urethane polymerization catalyst, such as noted in areas 14B' in Figure II, the corresponding portions of the surface of the urethane top coating composition lying directly thereover will have a raised or expanded chemically embossed height and will have a dead, dull, low gloss effect, such as noted in areas 18B'.
It is therefore to be appreciated that all four types of surfaces areas of the urethane top coating composition are possible in any one particular product, pending upon the particular predetermined pattern or design of the printing ink composition selected, thereby providing excellent choices of the four above-described surfaces.

The present invention will be described further with particular respect to the following specific examples, wherein there are shown preferred and typical embodiments of the present invention. However, such specific examples are primarily illustrative of the general principles of the present invention and the specific materials, chemical compounds, patterns or designs and other particular aspects of the invention should not be construed as limitative of the broader scope of the inventive concept, except as defined by the scope and the spirit of the appended claims.

**EXAMPLE I**

A resinous polymer sheet material, such as illustrated in Figure I of the drawings, is made as follows:

The backing sheet material comprises a relatively flat, 0.030 inch thick fibrous sheet of felted asbestos fibers with an acrylic smoothing or leveling coating thereon.

The asbestos fibrous backing sheet material is coated substantially uniformly to a wet thickness of about 0.012 inch with the following potentially foamable base resinous polymer composition:
Polyvinyl chloride, med. mol. wt., general purpose dispersion resin, inh. vis. 0.99 (ASTM D-1243-66) 30.2
Polyvinyl chloride, med. mol. wt., dispersion grade resin, inherent viscosity 1.0 8.2
Polyvinyl chloride, med. mol. wt., blending resin, inherent viscosity 0.9 17.1
Anhydrous alumina silicate filler 6.9
Butyl benzyl phthalate plasticizer 15.4
Alkyl benzyl phthalate low boiling point plasticizer 9.3
Polydodecyl benzene 7.4
Azodicarbonamide blowing or foaming agent 1.1
Accelerator/stabilizer 0.4
Titanium dioxide 2.5
Diocetyl phthalate 1.5
Wetting agent 0.03

Gelling and firming of the potentially foamable base resinous polymer composition is accomplished in an oven atmosphere maintained at an elevated temperature of about 300°F. for a time of about 3 minutes. This temperature is not sufficiently high as to activate or decompose the blowing or foaming agent.

The gelled and firmed, potentially foamable base resinous polymer composition is then printed with a ceramic tile brick pattern or design as shown in Figure 1, as follows:

Areas 14A are printed with the following ink compositions:
Solution grade co-polymer of vinyl chloride (90 Parts) and vinyl acetate(10 Parts) 14
Methyl ethyl ketone 81
Blowing or foaming inhibitor 0
Dibutyl tin dilaurate urethane polymerization catalyst 5
Coloring pigment or agent, as required or desired

The printed, gelled, potentially foamable base resinous polymer composition is then allowed to dry and a resinous wear layer composition is applied thereto to a wet thickness of about 0.010 inch and having the following composition:

Polyvinyl chloride, dispersion grade, inh. vis. 0.8 100
Butyl benzyl phthalate plasticizer 28
2,4,4-trimethyl pentyl-3,5-diisobutyrate 23
Alkyl benzyl -thalate 4
Ba-Zn phosphite heat stabilizer 6

Gelling or firming, blowing or foaming, and fusion of the resins take place by heating in an oven atmosphere at an elevated temperature of about 430°F. for a period of about 1 minute and 40 seconds.

The blown or foamed, fused, chemically embossed, resinous polymer sheet material is then coated with a urethane top coating composition to a substantially uniform thickness of about 1½ mils and having the following formulation:
Methylene-bis (cyclohexylisocyanate), 31.8%
minimum NCO-content 85.8
Polytetramethylene ether glycol, hydroxyl
number 174, molecular weight 650 9.8
Polyoxy alkylene polyether tetrol, hydroxyl
number 374, molecular weight 600 69.0
Reactive silicone wetting agent, hydroxyl
number 47, molecular weight 2400 0.12

Polymerization or curing of the applied urethane
top coating composition takes place in an oven atmosphere
having an elevated temperature of about 325°F. for about
5 minutes. The relatively lower mortar or grout areas
18A lying directly over the inhibitor containing areas
14A of the printing ink composition are uncured and are
soft, fluid or semi-fluid. The relatively higher land areas
18B lying directly over the catalyst-containing areas
14B of the printing ink composition are cured, hardened
or firmed and have a smooth, shiny, high gloss.

The product, upon cooling, is passed through
the nip of a silicone rubber roll under pressure which re-
sults in a surface of reduced gloss.

Then an additional amount of dibutyl tin
dilaurate urethane polymerization catalyst is applied
onto the product, such as by spraying a 1/4 to 1% solution
of the catalyst in tertiary butyl alcohol.

Passage through an oven atmosphere at an
elevated temperature of about 325°F. for 3 minutes cures
the urethane top coating composition in those areas 18A
which now become hardened and firmed but which acquire
a dull or matte appearance due to the embossing which is
retained in these areas to produce a roughened or pebbled appearance having a low gloss effect but which is not retained in areas 18B which revert to their previous glossy appearance.

The differential gloss effect of the contrast of the raised, chemically embossed, shiny, high gloss areas 18B with the normal height, chemically unembossed, dull, dead, low gloss areas 18A is unusual and most interesting. Substantially perfect registry is noted between the areas of the ink composition, as well as with the substantially perfect registry of the areas 18B of the urethane top coating composition with the printed areas 14 B of the ink composition, with all areas in perfect registry with the chemically embossed relatively higher and lower portions. A very realistic mortar or grout appearance in the relatively lower, normal height areas, as contrasted with the very realistic land appearance of the relatively higher, chemically embossed areas. Substantially all the monomeric material originally in the top coating composition are polymerized or cured. There is substantially no free monomer in the final top coating. The resinous polymer sheet material product finds excellent use as a resilient floor covering. In such use, the facts that the polyurethane top coating is polymerized and/or cross-linked in all portions, and is thermoset is highly advantageous, in that such surfaces are more resistant to changes under future conditions.
EXAMPLE II

The procedures described in Example I are followed substantially as set forth therein, with the exception that the printing ink composition are changed, in order to prepare the resinous polymer sheet material product illustrated in Figure II.

The printing ink composition which is applied to areas 14A' contains both a blowing or foaming inhibitor, as well as a urethane polymerization catalyst, as follows:

<table>
<thead>
<tr>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution grade co-polymer of vinyl chloride (90 Parts) and vinyl acetate (10 Parts)</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>Trimellitic anhydride</td>
</tr>
<tr>
<td>Dibutyl tin dilaurate</td>
</tr>
<tr>
<td>Pigment or colorant, as required or desired</td>
</tr>
</tbody>
</table>

The printing ink composition which is applied to areas 14B' contains neither a blowing or foaming agent nor a urethane polymerization catalyst, as follows:

<table>
<thead>
<tr>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution grade co-polymer of vinyl chloride (90 Parts) and vinyl acetate (10 Parts)</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>Pigment or colorant, as required or desired</td>
</tr>
</tbody>
</table>

The differential gloss effect of the contrast of the normal height, chemically unembossed, shiny, high gloss areas 18A' with the relatively higher, chemically embossed, dull, dead, low gloss areas 18B' is unusual and most interesting. Substantially perfect registry is noted between the areas 18A' of the urethane top coating with the areas 14A' of the printing ink composition. And,
substantially perfect registry is noted between the areas 18B' of the urethane top coating composition with the areas 14B' of the printing ink composition. The results of this Example are generally comparable to the results obtained in Example I, as more specifically described in greater detail therein.

**EXAMPLE III**

The procedures described in Example I are followed substantially as set forth therein, with the exception that the methylene-bis-(cyclohexylisocyanate) is replaced by isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate. The results of this Example are generally comparable to the results obtained in Example I.

**EXAMPLE IV**

The procedures described in Example I are followed substantially as set forth therein, with the exception that the methylene-bis-(cyclohexylisocyanate) is replaced by 2,4,4-trimethyl-hexamethylene diisocyanate. The results of this Example are generally comparable to the results of Example I.

**EXAMPLE V**

The procedures described in Example I are followed substantially as set forth therein, with the exception that the ink composition used in print areas 14B has the following composition:

<table>
<thead>
<tr>
<th>Components</th>
<th>Parts</th>
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<tbody>
<tr>
<td>Solution grade co-polymer of vinyl chloride (90 Parts) and vinyl acetate (10 Parts)</td>
<td>13.5</td>
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<tr>
<td>Methyl ethyl ketone</td>
<td>79.5</td>
</tr>
<tr>
<td>Dibutyl tin dilaurate</td>
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<tr>
<td>Pigment or colorant, as required or desired</td>
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</table>
The results of this Example are generally comparable to the results of the procedures of Example I, as more specifically described therein. The urethane top coating composition of the final resinous polymer sheet material is substantially cured or polymerized in all portions thereof and is substantially monomer free in all portions. All portions are thermoset and have relatively high melt viscosities.
WHAT IS CLAIMED IS:

1. A differential gloss resinous sheet material comprising: a base resinous material, portions of which are blown or foamed and portions of which are unblown or unfoamed; a printing ink composition on said base resinous material in the form of a predetermined pattern or design, some printed portions of which contain a urethane polymerization catalyst and some printed portions of which contain a blowing or foaming inhibitor, said urethane polymerization catalyst-containing portions and said blowing or foaming inhibitor-containing portions occupying the same or different portions; a resinous wear layer applied to said printing ink composition and having relatively higher areas and relatively lower areas; a substantially monomer-free polyurethane top coating, substantially all parts of which are substantially completely polymerized, applied to said resinous wear layer and having relatively higher surfaces and relatively lower surfaces, some of said surfaces having a smooth, shiny, high gloss appearance and some of said surfaces having a dead, dull, low gloss appearance.

2. A differential gloss resinous sheet material as defined in Claim 1, wherein said relatively higher surfaces have a smooth, shiny, high gloss appearance.

3. A differential gloss resinous sheet material as defined in Claim 1, wherein said relatively higher surfaces have a dead, dull, low gloss appearance.

4. A differential gloss resinous sheet material as defined in Claim 1, wherein said relatively lower surfaces have a smooth, shiny, high gloss appearance.

5. A differential gloss resinous sheet material as defined in Claim 1, wherein said relatively lower surfaces have a dead, dull, low gloss appearance.
6. A method of making a differential gloss resinous sheet material which comprises: forming a gelled, potentially foamable, base resinous material containing a blowing or foaming agent; applying to said gelled, base resinous material a printing ink composition in a predetermined pattern or design, some printed portions containing urethane polymerization catalysts and some printed portions containing blowing or foaming inhibitors, said urethane polymerization catalyst-containing printed portions and said blowing or foaming inhibitor-containing printed portions occupying the same or different printed portions; applying substantially uniformly to said printed, gelled, base resinous material a substantially uniform resinous wear layer; applying heat to said base resinous material and said resinous wear layer to gel and fuse said resinous wear layer and to blow or foam and fuse said base resinous material; applying a substantially uniform urethane top coating composition comprising unreacted polyols and unreacted polyisocyanates substantially uniformly to said resinous wear layer; applying heat to said base resinous material, said resinous wear layer and said urethane top coating composition to polymerize the unreacted polyols and unreacted polyisocyanates only in those surface portions of the urethane top coating composition lying directly over said urethane polymerization catalyst-containing printed portions of said printing ink compositions, whereby such surface portions become relatively hardened whereas the other surface portions of said urethane top coating composition remain relatively soft and tacky and substantially unpolymerized; mechanically embossing the entire urethane top coating to cause texturing of the unpolymerized surface; applying a urethane polymerization catalyst substantially uniformly to the entire surface of
said urethane top coating composition; and applying heat to said thus-texturized urethane top coating composition without the urethane catalyst thereon, whereupon said unpolymerized surface portions thereof become polymerized but retain the dead, dull, low gloss surface portions due to said mechanical embossing and the previously polymerized portions revert back to their original smooth, shiny, high gloss appearance.

7. A method of making a differential gloss resinous sheet material as defined in Claim 6, wherein said urethane polymerization catalyst and said blowing or foaming inhibitor are included in the same portions of said printing ink composition.

8. A method of making a differential gloss resinous sheet material as defined in Claim 6, wherein said urethane polymerization catalyst and said blowing or foaming inhibitor are included in different portions of said printing ink composition.

9. A method of making a differential gloss resinous sheet material as defined in Claim 6, wherein substantially all the portions of said urethane top coating composition is polymerized and is substantially monomer-free.

10. A method of making a differential gloss resinous sheet material as defined in Claim 6, wherein said urethane polymerization catalyst is applied to the entire surface of the urethane top coating before mechanically embossing said coating.
INTERNATIONAL SEARCH REPORT

International Application No. PCT/US83/01204

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 1

According to International Patent Classification (IPC) or to both National Classification and IPC

- IPC 3B 32B 3/30; B05D 3/02
- US 427/270, 273; 428/159, 201

II. FIELDS SEARCHED

Minimum Documentation Searched 4

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Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched 4

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

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<th>Category</th>
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<td>US, A 4187131 (5 February 1980) Congoleum Corporation; entire columns</td>
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* Special categories of cited documents: 15

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 1 2

18 October 1983

International Searching Authority 1

ISA/US

Date of Mailing of this International Search Report 2

21 OCT 1983

Signature of Authorized Officer 19

W. G. [Signature]

Form PCT/ISA/1 (second sheet) (October 1981)