

United States Patent

[11] 3,616,176

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 [21] Appl. No. **681,231**
 [22] Filed **Nov. 7, 1967**
 [45] Patented **Oct. 26, 1971**
 [73] Assignee **General Mills, Inc.**

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[54] **POLYAMIDE DECAL**
7 Claims, 2 Drawing Figs.

[52] U.S. Cl. **161/165,**
 161/167, 161/406, 156/240, 117/3.4

[51] Int. Cl. **B44c 1/16,**
 C09j 7/00

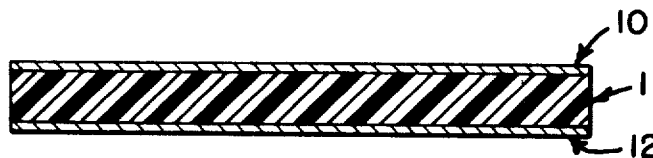
[50] **Field of Search** 117/3.4,
 36.1; 161/167, 165; 156/230, 231, 240;
 260/404.5, 407, 18 N, 37 N

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ABSTRACT: There is disclosed a dry thermal transfer decal consisting of a single polyamide film having decoration thereon which film serves as a carrier for the decoration, a protective coating for the decoration and the adhesive layer. The polyamide is the thermal amidification product of essentially equivalent amounts of a polymeric fat acid having a dimeric fat acid content greater than 80 percent by weight and of a diprimary diamine.



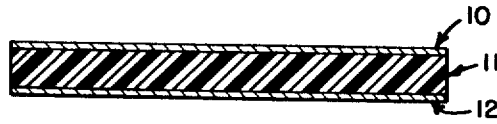


FIG. 1

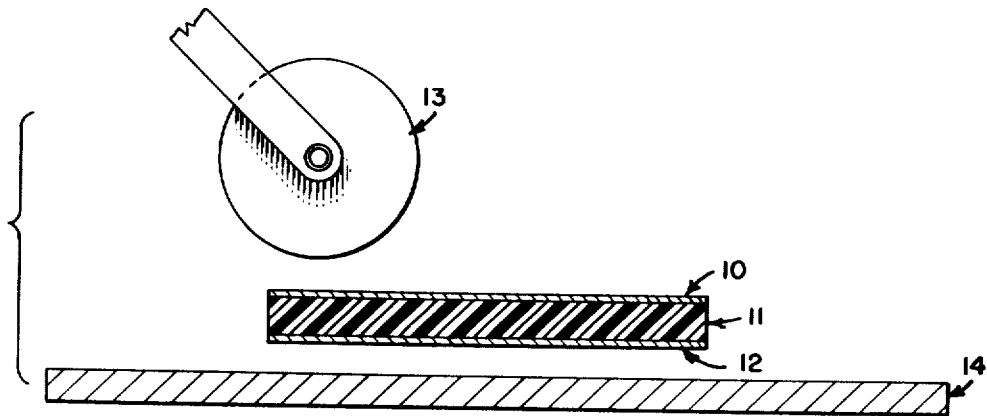


FIG. 2

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POLYAMIDE DECAL

This invention relates to decals employing polymeric fat acid polyamides as a transfer structure. The polymeric fat acids having a dimeric fat acid content of at least 80 percent by weight. These polyamides possess a combination of properties which permit utilization in virtually all types of hot transfer equipment and application to a large variety of substrates. Thus the decal of the present invention has general overall application in the decorative barriers, decorative or printing field whereas other types of decals have only limited application.

FIG. 1 shows an enlarged diagrammatic view of a preferred complete decal structure of the present invention.

FIG. 2 illustrates diagrammatically a simplified version of effecting transfer by utilization of thermal energy to a substrate.

Essentially the decal comprises a release sheet 10, a polymeric fat acid polyamide layer 11 to which is applied a decorative layer 12, layers 11 and 12 forming the transfer structure. The decal is a dry transfer one which means that no soaking of the decal in a liquid such as water is necessary to transfer the decorative material to the substrate to which it is to be applied. Because of the nature of the polyamide employed, the decal is a hot transfer label by which is meant that thermal energy is required to effect transfer of the decorative material.

In FIG. 2, there is shown diagrammatically a simple version of application of the decal to the substrate. In this version a thermal energy source 13 shown as a heated roller, is employed to transfer the decal comprising 10, 11 and 12 to the substrate 14. In this version, the decal is brought into contact with the substrate 14 and the heated roller applied to the decal for a time sufficient to heat seal the decal to the substrate. The time period is not critical and in most instances is measured in few seconds. It is important, however, that the heat be applied so that the polyamide layer is heated near or above its softening point so that the layer may be heat sealed or fused to the substrate. Upon withdrawal of the heat source, the polyamide layer quickly cools to a temperature below its softening point and the release sheet is removed, the polyamide layer with the decorative layer being bonded, fused or sealed to the substrate. In some use applications, the release sheet may be dispensed with, such as applications in which the thermal energy or heat source will not come into direct contact with the decal. In instances where direct contact of the heat source or where application of pressure is necessary, a release sheet may be necessary.

In this invention, the polyamide layer acts as the decorative or printing material acceptor or carrier, the adhesive layer and a coating layer which protects the decorative layer. In decals of the past, it was common to use a separate layer upon which the decorative material was applied, and/or a separate adhesive layer and/or a separate protective coating layer. In this invention, the polyamide layer serves all three functions. Further, while the decals are decorative to the eye, they may also perform functionally as a barrier for gas permeability, such as for nitrogen gas. Where this barrier function is important or desirable, the decal is applied over the whole or major part of the container wall or substrate, as an overlay. Thus both a decorative and functional film is applied.

The decals find particular utility in the container field, of interest to the producer, decorator and packer of conventional containers such as blow-molded containers or prefabricated containers such as boxes, bottles or tubes. The decal will also find use as a label to provide a clear printed or other decorative layer to any items, including, but not limited to, identification catalog indicia on books in libraries or decorative protective covers for books, and on virtually any item desired since the polyamide layer will bond to metal, wood, leather, paper, plastics such as vinyl, polyethylene, polypropylene. The particular polyamide layer employed, of course, will be selected for the optimum adhesion properties to the desired item.

The invention will therefore be useful in any industry where decorative or printed material is found on the items such as

gift papers, sporting goods, appliances, automotive, shoe and luggage, furniture, publishing and stationery, apparel and haberdashery.

The decal provides a total container or labeling service technology in a market where customers require surfaces exposed to wear and abuse, a multiplicity of colors and shapes, adhesion to substrates hard to decorate, daily short production runs, flexibility in high speed applications and favorable economics for decorating disposable items.

As indicated, the polyamide layer is the acceptor or carrier for the decorative material whether the decorative material be a continuous uninterrupted surface or a discontinuous surface such as in printing. The polyamide layer itself may be clear, virtually water white or may be dyed or colored to provide a colored but clear and transparent layer or it may be an opacified layer. A wide variety of printing methods may be employed as the polyamide layer is receptive to a wide range of inks of varying properties. Accordingly, there may be employed offset methods, lithographic, rotogravure or flexographic printing techniques.

As indicated the decal may be transferred to the finished object or package or during fabrication of the item such as blow-molded containers where there is fusion with the substrate. Hot-stamping presses, a relatively high-pressure method, may be employed for application of the decal. Also low-pressure methods such as hot roller or hot air contacts may be employed. The hot-roller method is exemplified in the drawing. Any conventional method or equipment, by which thermal energy may be applied to the decal, may be employed.

Briefly, the decal is formed by applying to the release sheet the polyamide layer upon which the decorative material may be then applied. The polyamide layer is preferably applied from a solution to the release sheets. Upon evaporation of the solvent, a continuous film is left on the release sheet. The polyamide may also be applied to the release sheet by extrusion of a continuous film thereon. Colors, dyes or opacifying agents may be included in the polyamide. Alternatively, the polyamide layer may comprise a fibrous material which has been impregnated with the polyamide, which impregnated fibrous material may then be applied to the release sheet either in its wet state directly after impregnation from a solution or by heat activation thereof prior to application to the release sheet. In these cases, the polyamide layer is a fibrous reinforced film. The fibrous material may be paper, glass fibers or textile materials, both natural or synthetic.

The release sheet or layer must be of such character that any bond formed between it and the polyamide layer to be transferred is sufficient to maintain the materials in place prior to the transferring operation and yet such bond must be sufficiently weak so as to clearly release from the polyamide layer during a transferring operation. Further, the surface of the release sheet preferably presents a smooth and shiny surface. Thus the release sheet or layer should show as little adhesion and cohesion as possible with the polyamide layer.

The exact specific material employed as the release sheet or layer will depend to some extent on the nature of the specific polyamide layer. For example, if the specific polyamide is one which bonds well to vinyl, polyethylene or polypropylene, such materials could not be employed as release sheets. With specific polyamides which exhibit poor adhesion to such materials, these materials could be employed as the release material or sheet. Generally, a paper coated or treated with a material that will provide little adhesion or cohesion to the polyamide layer is preferred. Illustrative thereof is a wax-laminated or adhesive-laminated paper where the heat-sealable material will melt at lower temperatures than the polyamide layer and, while molten, will exhibit substantially complete lack of adhesion, cohesion or compatibility with the polyamide transfer layer. A conventional type release coating such as a silicone coating, silicone polymer of silene, may be employed provided it does not exhibit affinity for or migrate to the polyamide side when the polyamide layer is applied from solution or, later on, when it is heat activated during the

transfer operation. Thermoplastic or thermosetting coating may be employed from which the polyamide layer will release at temperatures below the sealing point of the coating material. Teflon (tetrafluoroethylene) coatings may be employed. The preferred form of release sheet is paper coated with a silicone.

As indicated above, the decal comprises a polymeric fat acid polyamide layer of polymeric fat acid having a dimeric fat acid content greater than 80 percent by weight to which is applied a decorative layer, Preferably the decal also has a release sheet or layer.

The polyamide resins accordingly employed in the present invention are the thermal condensation or amidification products of a polymeric fat acid having a dimeric fat acid content greater than 80 percent by weight and preferably greater than 90 percent by weight and an aliphatic, cycloaliphatic or aromatic diprimary diamine. The polyamides are prepared by conventional amidification procedures, which usually include heating at temperatures between 100° and 300° C., preferably 200° to 275° C., for a time sufficient to complete reaction usually about 2 to 8 hours and most usually about 4 to 6 hours. The reaction is generally conducted while removing the byproduct water of reaction.

Polymeric fat acids are well known and commercially available. One method of preparation of polymeric fat acids can be seen in U.S. Pat. No. 3,157,681. The preparation of very light-colored polymeric fat acids and polyamides thereof which are preferred for use in the present invention can also be seen from U.S. Pat. No. 3,256,304.

Typical compositions of commercially available polymeric fat acids, based on unsaturated C₁₈ fat acids (tall oil fatty acids) are

C ₁₈ monobasic or monomeric fat acids (monomer)	5-15% by weight
C ₃₆ dibasic or dimeric fat acids ("dimer")	60-80% by weight
C ₅₄ (and higher) polybasic or trimeric fat acids ("trimer")	10-35% by weight

While the foregoing commercially available product is prepared by polymerization of unsaturated fatty acids in tall oil fatty acids, similar polymeric fat acids may be prepared from other monobasic or monocarboxylic aliphatic acids, naturally occurring or synthetic, having hydrocarbon chains or eight to 24 carbon atoms which will be referred to herein as a fat acid or monomeric fat acid.

The relative ratios of monomer, dimer and trimer in such unfractionated polymeric fat acids are dependent on the nature of the starting material and the conditions of polymerization. For the purposes of this invention, the term monomeric fat acids refers to the unpolymerized monomeric acids, the term dimeric fat acids refers to the dimer of the fat acids and the term trimeric fat acids refers to the residual higher polymeric forms consisting primarily of trimer acids but containing some higher polymeric forms. The term polymeric fat acids as used herein is intended to be generic to polymerized acids obtained from fat acids and consists of a mixture of monomeric, dimeric and trimeric fat acids.

The saturated fat acids are generally polymerized by somewhat different techniques than those described in U.S. Pat. No. 3,157,681, but because of the functional similarity of the polymerization product, they are considered equivalent to those prepared by the methods described as applicable to the ethylenically and acetylenically unsaturated fat acids. While saturated acids are difficult to polymerize, polymerization can be obtained at elevated temperatures with a periodic catalyst such as di-t-butyl peroxide. Because of the generally low yields of polymeric products, these materials are not currently commercially significant. Suitable saturated fat acids include branched and straight chain acids such as caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, isopalmitic, stearic acid, arachidic acid, behenic acid, and lignoceric acid.

The ethylenically and acetylenically unsaturated fat acids which may be polymerized and their method of polymerization are described in the above mentioned U.S. Pat. No. 3,157,681.

Reference has been made hereinabove to the monomeric, dimeric and trimeric fat acids present in the polymeric fat acids. The amounts of monomeric fat acids, often referred to as monomer, dimeric fat acids, often referred to as dimer, and trimeric or higher polymeric fat acids, often referred to as trimer, present in polymeric fat acids may be determined analytically by conventional gas-liquid chromatography of the corresponding methyl esters. Another method of determination is a micromolecular distillation analytical method. This method is that of R. F. Paschke et al., J. Am. Oil Chem. Soc., XXXI (No. 1), 5, (1954), wherein the distillation is carried out under high vacuum (below 5 microns) and the monomeric fraction is calculated from the weight of product distilling at 155° C., the dimeric fraction calculated from that distilling between 155° C. and 250° C., and the trimeric (or higher) fraction is calculated based on the residue. Unless otherwise indicated herein, the chromatography analytical method was employed in the analysis of the polymeric fat acids employed in this invention and all limitations on dimeric fat acid content herein are based on this method. When the gas-liquid chromatography technique is employed, a portion intermediate between monomeric fat acids and dimeric fat acids is seen, and is termed herein merely as intermediate, since the exact nature thereof is not fully known. For this reason, the dimeric fat acid value determined by this method is slightly lower than the value determined by the micromolecular distillation method. Generally, the monomeric fat acid content determined by the micromolecular distillation method will be somewhat higher than that of the chromatography method. Because of the difference of the two methods, there will be some variation in the values of the contents of various fat acid fractions. Unfortunately, there is no known simple direct mathematical relationship correlating the value of one technique with the other.

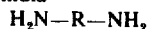
As earlier indicated, the preferred polyamides employed in the present invention are those in which the polymeric fat acids employed to prepare the polyamides used in this invention have a dimeric fat acid content in excess of 80 percent by weight and preferably in excess of 90 percent by weight since these resins have higher molecular weights. Such polymeric fat acids are obtained by fractionation by suitable means such as high vacuum distillation or by solvent extraction techniques from polymeric fat acids having lower dimeric fat acid contents, such as the common commercially available products described earlier.

In order that the polymeric fat acid polyamides have the properties desired for this invention, it is generally preferable that the polymeric fat acids employed have a dimeric fat acid content greater than about 80 percent by weight, more preferably above 90 percent by weight and most desirably in excess of 95 percent by weight. This preference arises as a practical matter due to the lack of necessity for trimer or monomer content control at the higher dimer contents to provide polyamides having the desired properties such as tensile strength and elongation. At dimeric fat acid contents about 95 percent by weight, virtually no control of trimer or monomer content is necessary. At the lowest dimeric fat acid contents, i.e., about 80 percent, it is preferred that the trimer to monomer ratio by weight be within the range of about 1:1 to 2:1. As the dimeric fat acid content increases, lesser control is needed and the range of the trimer to monomer ratio widens to the point where virtually no attention is required when the dimeric fat acid content approaches values above 95 percent by weight. At a dimeric fat acid content of about 85 percent by weight, it is preferred that the trimer to monomer ratio be within the range of about 0.6:1 to 4.0:1. At about 90 percent dimeric fat acid content, this ratio preferably lies in the range of about 0.3:1 to 10:1. Of course, under idealized conditions, such as 100 percent dimeric fat acid content, there is no

trimer or monomer and the ratio thereby varies theoretically from 0 to infinity.

The polyamides are prepared by reacting the polymeric fat acids with a diamine. The resins may also include other copolymerizing acid and amine components and the copolymerizing acids or diamines employed may be a single diamine or a mixture of two different copolymerizing reactants. In addition, small amounts of monomeric, monocarboxylic acids may be present. With regard to any of the acid components, any of the equivalent amide-forming derivatives thereof may be employed, such as the alkyl and aryl esters, preferably alkyl esters having from one to eight carbon atoms, the anhydrides or the chlorides.

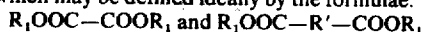
The diamines employed may be aliphatic, cycloaliphatic or aromatic diprimary diamines, which may be ideally represented by the formula



where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon radical preferably having from two to about 40 carbon atoms. Representative of such diamines are ethylene diamine, 1,2-diamino propane, 1,3-diamino propane, 1,3-diamino butane, tetramethylene diamine, pentamethylene diamine, hexamethylene diamine, decamethylene diamine, octadecamethylene diamine, metaxylylene diamine, paraxylylene diamine, cyclohexylene diamine, bis-(aminoethyl)-benzene, cyclohexane-bis-(methyl amine,) diamino-dicyclohexyl methane, methylene dianiline, piperazine, dimethylpiperazine, and dimeric fat diamine. The diamine may be employed alone or mixtures of two or more may be employed. The most preferred diamines are the alkylene diamines in which the alkylene group has from two to six carbon atoms and mixtures thereof with dimeric fat diamine (preferably having 36 carbon atoms).

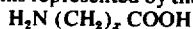
The dimeric fat diamine, sometimes referred to as dimer diamine, dimeric fat amine, or polymeric fat acid diamine are the diamines prepared by amination of dimeric fat acids. Reference is made thereto in U.S. Pat. No. 3,010,782. As indicated therein, these are prepared by reacting polymeric fat acids with ammonia to produce the corresponding nitriles and subsequently hydrogenating the nitriles to the corresponding amines. Upon distillation, the dimeric fat diamine is provided which has essentially the same structure as a dimeric fat acid except that the carboxyl groups are replaced by $-\text{CH}_2\text{NH}_2$ groups. Further, this diamine is also described in Research and Development Products Bulletin, CDS 2-63 by General Mills, Inc., June 1, 1963, as "Dimer Diamine" illustrated by the formula $\text{H}_2\text{N}-\text{D}-\text{NH}_2$ where D is a 36-carbon hydrocarbon radical of a dimeric fat acid.

The copolymerizing compounds commonly employed are aliphatic, cycloaliphatic or aromatic dicarboxylic acids or esters which may be defined ideally by the formulae:

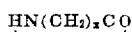


where R' is an aliphatic, cycloaliphatic or aromatic hydrocarbon radical preferably having from one to 20 carbon atoms and R₁ is hydrogen or an alkyl group (preferably having from one to eight carbon atoms.) Illustrative of such acids are oxalic, malonic, adipic, sebacic, suberic, pimelic, azelaic, succinic, glutaric, isophthalic, terephthalic, phthalic acids, naphthalene dicarboxylic acids and 1,4- or 1,3-cyclohexane dicarboxylic acid.

Other copolymerizing reactants may be amino acids or the corresponding lactams represented by the following formula



where x is an integer from 2 to 15, the corresponding lactams being represented by the formula



In general, the most common amino acids or corresponding lactams are aminocaproic acid (or epsilon caprolactam), aminoundecanoic acid and omega capryllactam where x is 5, 10, and 7 respectively.

Other difunctional coreactants are the monoalkanol amines which may ideally be represented by the formula



where R'' is a divalent aliphatic hydrocarbon radical, desirably having from two to eight carbon atoms and preferably an alkylene radical having from two to eight carbon atoms such as monoethanolamine, propanolamine, butanolamine, 2-amino-3-hexanol, 2-amino-4-pentanol, 5-amino-4-octanol, 3-amino-3-methyl-2-butanol. Where an alkanol amine is employed, a polyester-polyamide product is provided.

Essentially molar equivalent amounts of carboxyl and amine groups are employed in preparing the polyamide. Where an alkanol amine is employed the carboxyl groups employed are essentially equivalent to the amine plus hydroxyl groups. Where copolymerizing dicarboxylic acids or amino acids are employed, it is preferred that the carboxyl groups from the polymeric fat acid should account for at least 50 equivalent percent of the total carboxyl groups present. Also, where an alkanol amine or amino acid is employed, it is preferable that the amine groups from the diprimary diamine or diamines should account for at least 50 equivalent percent of the total amine groups present.

The following examples will serve to more clearly illustrate the invention. In these examples, the polymeric fat acid was derived from tall oil fatty acids by polymerization of tall oil fatty acids which are composed predominantly of a mixture of linoleic and oleic acids.

EXAMPLE I

There was cast from a solution-roller coater a polyamide resin directly onto a silicone treated bleached Kraft (40 lb./ream) release paper. The solution was a 25 percent solids of polyamide in a solvent system of isopropanol, toluene and water in a weight ratio of 50:40:10 respectively. This was done at room temperature (72° F.) with a feed and metering rolls spread of 8 mils. The resin coated release paper was then dried by blowing hot air (under 200° F.).

The polyamide resin was the thermal condensation product at a temperature of 440° F. for a period of 6 hours of a mixture of 132 pounds (4.46 eq.) of ethylene diamine and 57 pounds (1.42 eq.) of 1,2-propylenediamine and 1,716 pounds (6.14 eq.) of a polymeric fat acid having the following analysis:

* % M (monomer)	0.8
* % D (dimer)	96.3
* % T (trimer)	2.9
I. V. (iodine value)	
A. V. (acid value)	195
S. V. (saponification value)	201

*Micromolecular distillation method—JAOS XXXI (No. 1), 5, 1954.

The polyamide resin had the following properties:

Softening point	100° C.
Acid value	9.7
Amine value	1.2
Viscosity at 210° C.	33.5
Color, 40% Solution	0.6-

After solvent evaporation a polyamide resin continuous dry film (1 mil thick) substantially water white in color was obtained. About 3 grams of dry resin produced 1,000 square cm.² of cast film. Samples of the product showed easy release or the resin from the release sheet.

Printing was applied to the resin layer by the offset method. The printing was in reverse, that is from right to left. In this form, the printing can be read when it is projected on a mirror. When applied to the substrate the printing can be read in the conventional manner.

The printed stock was then heat sealed to the base material or substrate (in this case paper and treated high density polyethylene.) The thermal energy source was an electric iron with the heating element set at 375° F. After applying heat to

the release sheet for 5-10 seconds with hand pressure the thermal source was removed. After cooling (a few seconds,) the release sheet was removed leaving the polyamide resin film fused to the substrate and a sharp enhanced print was obtained. The polyamide resin film acts as a decorative or print protecting surface as well as the bonding agent to the substrate.

EXAMPLE II

In this example, decals were formed of a one-half mil film of the same polyamide and on the same release sheet as in example I and tested with various substrates. In this instance a dye was added to the resin solution resulting in a whiter film than example I without impairing transparency of the material. The dye was GAF heliogen blue, B. C. toner 56-6 001 and was added in an amount of 0.1 percent based on the solids content of the resin solution. The results on application to the various substrates can be seen from the following table.

TABLE I

Substrates	Applica- tion tem- perature, ° F.	Pressure, lbs./ sq. in.	Dwell cycle, sec.	Label ad- hesion to substrate after cooling
Polypropylene film:				
Treated.....	225-250	20	2	Good.
Untreated.....	225	20	2	Do.
Cast.....	225	20	2	Do.
Polyethylene:				
Treated.....	225-250	20	2	Do.
Filled treated.....	225	20	2	Do.
Polyvinyl chloride:				
Plasticized film.....	225-400	20	1-4	None.
Foam.....	225	2	3-4	Good.
Polycarbonate film.....	325	20	3	Do.
Polyvinylfluoride film.....	275	20	3	Do.
Polyethylene tereph- thalate film.....	350	20	3	Do.

EXAMPLE III

Decals were prepared with a 1-mil thick polyamide layer on the same release sheet as in example I. The polyamide resin layer was cast in the release sheet in the same manner as example I employing a 20 percent solution of the polyamide in a solvent mixture of isopropanol, toluol and water in a weight ratio of 40:32:8 respectively. In this instance, the polyamide was the thermal condensation product at a temperature of 250° C. for about 8 hours of 1.61 equivalents of polymerized tall oil fatty acids having the following analysis:

% M	0.5
% I	5.4
% D	88.6
% T	2.5
A. V.	195.3
S. V.	197.6
I. V.	101.8

0.80 equivalents of sebacic acid, 1.25 equivalents of ethylenediamine and 1.25 equivalents of 1,3-di(4-piperidyl) propane.

The polyamide had the following properties:

Acid Value	0.7
Amine Value	6.4
Ball & Ring Softening Point °C.	138
Tensile Yield	392
Tensile Strength	728
% Elongation	820

The decals were applied to polystyrene, polyethylene and flexible polyvinyl chloride substrates using a roll-stamping automatic equipment with flat surface dies instead of letter dies under the following conditions:

Thermostat temperature	375°-400° F.
Die temperature	350°-375° F.
Pressure	40 lbs. on 1 in. by 2 in. surface
Dwell time	2 seconds

In each instance a satisfactory hot transfer was achieved with adhesion to the substrates.

EXAMPLE IV

In this example a fibrous impregnated film was employed as the polyamide layer. The fibrous material was a sheet of 7.5-inch by 11-inch paper to which printing had been applied by offset method.

This paper was submerged into a 30 percent solids solution of a polyamide resin in a 50:50 mixture of toluol and isopropanol. After the paper was completely wetted with the resin it was air dried for about 2 hours at 95° F. and 50 percent relative humidity.

The polyamide employed was the thermal amidification product at 225° C. for about 3 hours, 16,790 gm. of polymerized tall oil fatty acids having the following analysis:

% M	0.8
% I	5.4
% D	88.6
% T	5.2
Acid Value	197
Saponification Value	201
Color (Gardner)	5-
% Unsaponifiables	0.1

and a mixture of 1,379 gm. of ethylene diamine and the diamine of polymerized tall oil fatty acids, said diamine having the following analysis:

Total Amine Value	186
Secondary and Tertiary Amine	14.7%
Color (Gardner)	5+
Iodine Value	94.2
% Nonamine	3.0%

The fiber reinforced printed polyamide film layer was then bonded to a treated polyethylene film substrate by placing the polyamide film over the substrate, placing a silicone release paper thereover and applying a thermal source thereto (an electric iron at 280° F.) for a few seconds. After cooling and removal of the release sheet, the printed decal or label was adhesively bonded to the polyethylene with the printing showing through the substantially transparent fiber reinforced polyamide layer.

The polyamide layer is preferably a cast film. The resin is cast onto the release sheet from a solution. When cast, solutions of from 50 to 15 percent solids of resin are employed, preferably about 25 percent. The solvents used will vary dependent on the particular polyamide resin. The solvent should be inert or nonreactive with the polyamide resin and where employed with the release sheet. The solvent should be volatile so that the cast film may be left in dry form ready for printing. The most advantageous solvents employed are alcohols, preferably aliphatic hydrocarbon alcohols having from two to six carbon atoms, such as ethanol, isopropanol, butanol, aromatic hydrocarbons, such as xylene and toluene; and mono- and dialkyl (two to six carbon atoms) ethers of ethylene glycol such as various cellosolves. The preferred solvents are isopropanol and toluene, particularly when employed in admixture with small amounts of water added, the most preferred being a mixture of 50 parts of isopropanol, 40 part of toluene and 10 parts of water.

The polyamide film thickness may desirably vary from about 0.1 mil to about 3.0 mil, preferably about 0.5 mil is the optimum film thickness for most applications.

In the hot transfer of the decal or label to the substrate, heat must be applied at or near the softening point of the polyamide layer, which will vary dependent on the particular polyamide employed. The preferred polyamides have softening points of about 70° to 180° C.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a dry thermal transfer decal consisting of a transfer structure having decoration thereon the improvement wherein said transfer structure consists of a single layer having a film thickness of about 0.1 to 3.0 mils of a thermoplastic polymeric fat acid polyamide having a softening point of from 70° C. to 180° C., said polyamide serving simultaneously as (a) a carrier for said decoration (b) a protective coating for said decoration and (c) the adhesive layer, said polyamide being the thermal amidification product at temperatures between 100° C. and 300° C. in which essentially equivalent amounts of carboxyl and amine are employed, or a polymeric fat acid having a dimeric fat acid content of greater than 80% by weight and a diprimary diamine of the formula $H_2N-R-NH_2$ where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon radical having from two to 40 carbon atoms.

2. A decal as defined in claim 1 wherein said polyamide

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layer comprises a continuous film of said polyamide.

3. A decal as defined in claim 2 wherein said polyamide layer comprises a fibrous material impregnated with said polyamide.

4. A decal as defined in claim 1 wherein said polyamide is the thermal amidification product of polymerized tall oil fatty acids and a mixture of ethylene diamine and diamino propane.

5. A decal as defined in claim 1 wherein said polyamide is the thermal amidification product of a mixture of polymerized tall oil fatty acids and sebacic acid and a mixture of ethylene diamine and 1,3-di(4-piperidyl)propane.

6. A decal as defined in claim 1 wherein said polyamide is the thermal amidification product of polymerized tall oil fatty acids and a mixture of ethylene diamine and a dimeric fat acid diamine.

7. A decal as defined in claim 1 and further comprising a release sheet on said transfer structure.