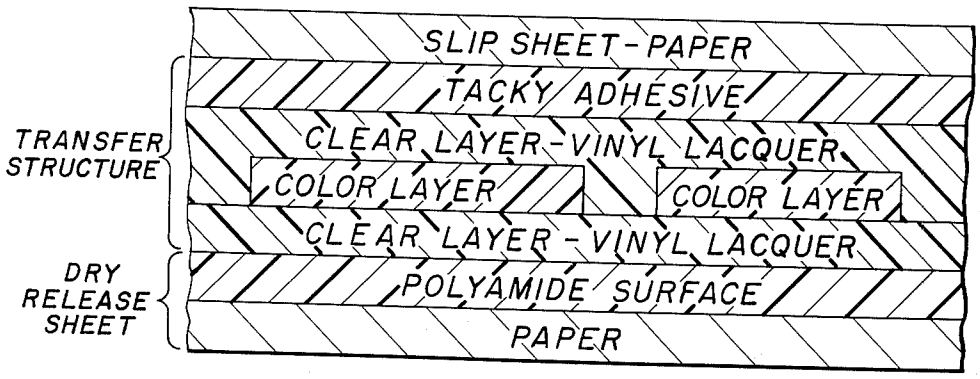
Nov. 20, 1962 J. D. AVELAR 3,065,120

DRY TRANSFER DECALS

Filed Aug. 29, 1960

FIG. 1.



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United States Patent Office 3,065,120 Patented Nov. 20, 1962

3,065,120

DRY TRANSFER DECALS

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Filed Aug. 29, 1960, Ser. No. 52,561
6 Claims. (Cl. 154—46.8)

This invention pertains to new and improved dry transfer decals.

The term "decal" is commonly used at the present time in place of the previously used term "decalcomania." Decals or decalcomanias are utilized in processes for placing designs or printing upon various types of surfaces. Originally virtually all decals were formed by coating a release sheet with a soluble composition and then by coating such composition with various lacquer, ink and other materials. With structures such as this it was necessary to soak the entire decal structure in a liquid, such as water, which would destroy the physical strength of the soluble release composition located upon the paper so that the "decal" could be removed from this paper and located upon the intended surface. So-called wet process decals of the type briefly indicated in the preceding paragraph unquestionably are satisfactory for many uses. Unfortunately, however, it is relatively expensive and time-consuming to utilize wet process decals, and as a result a number of attempts have been made to develop decals of a so-called dry transfer type.

Dry transfer decals as a general rule have included a so-called dry release sheet having a coated surface which holds the various materials which are transferred during the use of the decal, and these materials in turn carry a tacky adhesive which is normally covered by a release type of slip or cover sheet designed to be removed from the adhesive prior to use of the decal. There has been considerable difficulty in developing suitable dry transfer decals of this type because of the fact a dry release sheet must function properly under virtually any and all normal conditions.

The surface of the dry release sheet in a decal which holds the various materials which are transferred during the use of this decal must be of such a character that a bond is formed between it and these transferred materials which is sufficient to hold these materials in place as the cover or release sheet used as a protective cover for the adhesive is pulled off this adhesive. Further, such a bond must be sufficiently weak so as to clearly release materials being transferred during a transferring operation. Further, the surface of this sheet located adjacent to the materials which are transferred using a decal must be "smooth" in a relative sense so that these materials will have a desired, relatively shiny appearance when located in place upon an intended receiving surface.

A number of efforts have been made developing dry release sheets for use in decals. By and large such prior sheets can be considered to be comparatively unsatisfactory for one or more reasons although large volumes or numbers of many of such sheets have been used. Frequently the prior dry release sheets have not been satisfactory because of a lack of temperature stability. Thus, for example, certain types of prior dry release sheets are of such a character that the bond between the materials located upon them, while perhaps satisfactory at certain temperatures, is practically missing at other temperatures within a normal range. In other cases, dry release sheets for decals have been unsatisfactory because of the surface appearance of the transferred material disposed from these sheets, and in still other cases prior dry release sheets have been unsatisfactory because of the fact that the bond between them and material intended to be transferred is so strong that it is relatively impossible

to obtain a release during the use of decals using these sheets. In some cases such a bond has been so weak that it does not seem to hold the parts of a decal together.

A broad object of this invention is to provide new and improved dry transfer decals which overcome many of the aforegoing and related limitations and disadvantages of prior art dry transfer decals. Another objective of this invention is to provide new and improved dry release sheets for dry transfer decals usage which may be separately sold as articles of commerce. A still further object of this invention is to provide sheets of this type which may be easily and inexpensively manufactured and which may be used in accordance with established techniques in coating complete dry transfer decals.

These and various other objects of this invention, including many specific advantages of it, will be more fully apparent from a detailed consideration of the remainder of this specification including the appended claims and the accompanying schematic drawing in which:

FIG. 1 shows an enlarged diagrammatic view of a complete decal structure of the present invention as it is sold as an article of commerce.

The accompanying drawing is primarly intended so as to clearly indicate the character of a preferred type of decal utilizing this invention. It will be realized, however, that the present invention may be utilized with decals incorporating layers or sheets which are different from the parts of this type indicated in this drawing.

As an aid to understanding this invention it can be stated in essentially summary form that it concerns dry transfer decals, each of which includes a dry release sheet having a polyamide surface which, in a decal of the present invention, holds the transfer structure in the decal, this transfer structure having a surface layer located against the polyamide surface, which is incompatible with it, which is polar in character and which has an interfacial surface tension or, stated in another way, which has a free surface energy which is of the same or nearly the same value as the interfacial surface tension or free surface energy of the polyamide surface on the dry release sheet at the time it is applied to this polyamide surface. With this type of structure a satisfactory release may be achieved by pressing an adhesive up on the transfer structure onto an intended receiving surface and rubbing the dry release sheet several times so as to secure an adequate bond between this adhesive and such a receiving surface. When such a bond has been established in accordance with this invention the dry release sheet employed may be easily pulled off the transfer structure.

This invention is best more fully explained by referring to the accompanying drawing. In the decal structure shown in this drawing the dry release sheet utilized consists of a paper base, preferably of a type known as "hard" paper, having a filled and calendered surface which is coated with a polyamide composition in accordance with this invention. In creating a complete decal shown it is possible to locate by known silk screen, printing or other techniques so-called a "clear" layer of a resinous or plastic character and then to surmount this layer by various color layers designed to represent intended indicia such as pictures or printing or the like and then to further coat these color layers in accordance with known processes by a further "clear" layer. In a dry transfer decal this last "clear" layer is surmounted by means of a conventional tacky adhesive.

The entire series of layers consisting of the clear, color and adhesive layers indicated in the drawing may be referred to as a "transfer structure" inasmuch as it is these layers which are released from a dry release sheet as described when the adhesive is pressed against a receiving surface and sufficient force is applied to the exposed surface of the dry release sheet so as to create

a satisfactory bond between this surface and the adhesive. In accordance with conventional practice a cover type of protective slip sheet as shown in the drawing is preferably located upon the adhesive so as to prevent it from sticking to various things prior to the decal structure shown being used.

The present invention is primarily concerned with the dry release sheet indicated in the drawing and the "clear" layer of the transfer structure shown which is located upon this dry release sheet. It is possible to modify the decal illustrated so that various color layers or the like may be used instead of the "clear" layer shown against the polyamide surface of a release sheet although this is not generally desired with the present invention since it is generally desired to utilize a protective "clear" covering over such color or similar layers. In order to practice the teachings of this invention it is necessary that any material or materials in contact with the polyamide surface of the release sheet possess the various properties indicated in the preceding brief summary of this invention.

A number of different dry release sheet structures may be employed with the present invention. In the preferred embodiment shown the dry release sheet is formed by coating so-called "hard" clay coated, calendered paper with a solvent solution of structurally closely related polyamide resins obtained by polymerizing linoleic acid and then by reacting it with ethylene diamine so as to obtain resins having a softening point within the range of from 90° to 115° C., an amine value of 3, a specific gravity of 0.98, an ash content of 0.05 percent by weight and a viscosity of from about 7–45 poises at 150° C. measured using a #2 spindle at 20 r.p.m. on a Brookfield viscometer.

The amount of solvent used in applying an amine resin of this type may, of course, be varied in accordance with conventional practice. Preferably a conventional solvent mixture is used. Further, preferably this solvent mixture is uniformly applied so that about a minimum of 6½ lbs. of resin covers 330 square yards of "hard" clay coated calendered paper. If less resin than this is employed it is considered that a commercially satisfactory gloss is not achieved on the surface of a dry release, probably as a result of the resin not completely covering the paper surface. Greater amounts of resin than this can, of course, be used in achieving a desired gloss but the use of such greater proportions of resin is not considered economic because of the costs involved. Less resin than is specified herein can be used in creating a dry release sheet which will "release" a transfer structure as herein described, but the use of such smaller amounts of resin is not considered desirable because of the commercial importance of a gloss on the surface of a release sheet. The amounts of resin required for other types of paper than the type specified above will, of course, be different than the amount specified in this paragraph because of difference in surface porosity.

In creating dry release sheets as indicated above it is, of source, necessary to remove from the surface of the paper any solvent used in applying the polyamide resin. This can be done in accordance with various known established processes. Preferably, however, it is done by heating a coated surface at above the boiling point of the solvents employed at a temperature at a maximum of about 15° C. over the melting point of the highest melting polyamide component used in coating the paper. Further, this heat is preferably applied only for a comparatively short period sufficient to "fuse" the resin present so as to securely bond all of this resin together and so as to create a relatively smooth surface coat upon it. No separate calendering or similar steps are necessary to create a surface coat of this type; it apparently results solely from the resin used "flowing" under the influence of heat. The amount of heat which may be applied will vary, of course, depending upon a number of circumstances, such as the nature of a heat source, the time during which heat is applied, etc. In general, the presence of overheating will be readily determined by the appearance of surface blisters, and the absence of sufficient heating may be determined by a lack of a desired "smooth" surface upon the polyamide material.

It is possible to form dry release sheets falling within the scope of this invention in a number of different ways. It will be recognized that polyamide resins as specified in the preceding discussion are created in accordance with the Bradley U.S. Patent 2,379,413 issued July 3, 1945. Various polyene fatty acids and their esters can be treated in accordance with the process set forth in this patent so as to be reacted with ammonia and various primary, secondary and alkyol amines so as to create polyamides which may be suitably employed with the present invention. Because of the fact that the term "fatty acids" has a well established meaning as may be determined by reference to standard texts, such as Hackh's "Chemical Dictionary," it is not considered necessary to set forth in this specification examples of all acids of this type which may be employed in creating polymers usable with this invention.

All of such resins are considered to be created by forming addition polymers of such fatty acids having terminal carboxyl groups and then by reacting them with amines as indicated. All of these resins are considered to conform to the following general formula in which:

$$HO\{OC—R—CONHR'—NH\}_nH$$

in which R is a hdyrocarbon group of indeterminate configuration. In the preferred type of resin as specified in the preceding such an indeterminate group is derived from linoleic acid and contains 34 carbon atoms; further, in the preferred resin specified in this preceding discussion R′ is the group $—CH_2CH_2—$ which, of course, is derived from ethylene diamine. Such resins in order to be used in the present invention can be applied to a suitable supporting sheet such as a paper sheet as specified in the preceding in several different known ways. For example, they may be applied from a solvent solution as previously indicated or they may be applied by so-called "hot melt" coating techniques or the like. In many cases, such resins can be formed into a continuous film capable of being used alone as a dry release sheet. Because of the nature of such resins their structural formulas, and their molecular weights will differ. For this reason and value *n* in the preceding structural formula is not separately specified in this specification; it is considered preferable, however, to have this value *n* of such a number that the resins used with this invention have melting points above normally encountered ambient temperatures and have the physical characteristics and properties indicated in the preceding discussion of forming a preferred dry transfer sheet of this invention.

A dry transfer sheet as herein specified may be coated with a clear and other layers of a transfer structure in accordance with known established processes using silk screen, printing or other various techniques. It is important, however, that any layer or layers of such a transfer structure placed in contact with the polyamide surface of the dry release sheet be incompatible with such a surface. Since the term "incompatible" has a well established technical meaning it is not considered necessary to define it specifically in this specification. Further, any such layer or layers in contact with the polyamide surface must be of a polar character and must have an interfacial surface tension, or expressed otherwise, a free surface energy which is substantially the same as the free surface energy or interfacial surface tension of the polyamide surface at the time of application to this polyamide surface. It will be realized that such polarity and such surface tension or energy are, of course, related in any given material. It will be realized also that such polarity of any layer or layers in contact with the poly-

amide surface is important because of the attraction of polar groups for one another. The polarity of such layer or layers is important as far as obtaining a satisfactory bond of a "controlled" or "balanced" type as is necessary for the satisfactory utilization of a dry transfer decal as herein explained.

Satisfactory results can be achieved using a material or materials for such a layer or layers in a transfer structure in which the free surface energies of such a material or materials at the time of application to a polyamide surface as herein described is such that the difference in free surface energies between the polyamide surface and such a material or materials is no greater than about 10 dynes per square centimeter. If the differential in values in free surface energies or interfacial surface tensions is greater than this amount, pocking and pin holes of the material or materials applied to a polyamide surface will tend to be apparent. Polyamide surfaces as used with this invention normally have free surface energies or interfacial surface tensions of less than 43 dynes per square centimeter and polyamide surfaces are preferably used which have free surface energies or interfacial surface tensions of from about 25 to about 35 dynes per square centimeter.

These values have been determined as a result of measurements on polyamide surface films by comparisons with liquids of known free surface energies or interfacial surface tensions placed upon these films. Suitable devices for measuring free surface energies or interfacial surface tensions are well known at the present time. Variations in values of interfacial surface tension or free surface energy are usually encountered depending upon the type of equipment used in making such measurements.

In general, if too great a variation in free surface energies or interfacial surface tensions are involved the two materials or compositions which are placed in contact with one another in locating a transfer structure in a decal on a dry release structure of this invention, a satisfactory initial coating of the transfer structure on the dry release structure is not achieved. In other words, the transfer structure does not tend to uniformly cover the dry release sheet. The permanent bond between these structures in accordance with this invention is at least a partial consequence of the polar character of a layer or layers directly in contact with a polyamide surface as herein specified and surface attraction exerted by polar groups.

A number of different known lacquers, inks or the like used in making conventional decalcomanias can be employed with such polyamide surfaces in accordance with this invention. Because of their polar character it is preferred to utilize with the present invention lacquers or inks or the like which are based upon polar resinous or polymer compositions using primary materials selected from the group consisting of cellulose esters, and ethers, acrylic polymers and vinyl chloride and acetate polymers and co-polymers. All of such materials are of a polymeric character and are incompatible with polyamide surfaces as herein explained.

Normally various lacquers, inks and the like such as the "clear" shown in contact with the polyamide surface in the drawing include various plasticizers, anti-oxidants, wetting agents and other similar ingredients. In determining whether or not a specific composition can or cannot be used with a polyamide dry release surface in accordance with this invention it is considered necessary to take into consideration the free surface tension or energy of such a composition as a "whole" including the secondary ingredients as specified above and not just the free surface energy of the polymeric and resinous material employed in such a composition alone. Frequently the type of bond achieved at a polyamide surface in accordance with this invention can be improved by utilizing a plasticizer or the like as specified in this paragraph which not only has an effect on free surface energy, but which also is of a polar character so as to aid in the formation and maintenance of a surface bond.

In order to facilitate understanding of this invention a satisfactory "clear" as indicated in the drawing upon a polyamide surface of a preferred character as specified in the preceding portions of this specification, this polyamide mixture having a free surface energy of about 30 dynes per square centimeter, can have a composition as follows:

Acrylic, methacrylic acid copolymer (equal molar proportions, mol. wt. about 10,000)_____gm__	50
Vinylchloride, vinyl acetate copolymer (70 mol. parts chloride, 30 mol parts acetate, mol. wt. 10,000–13,000) _____gm__	50
Sebacic acid-ethylene glycol polyester polymer (mol. wt. about 2,200)_____gm__	26
Cyclohexanone _____gm__	100
Isopherone _____gm__	80

Of course, after such a "clear" composition is applied to a polyamide surface as specified the solvents within it are removed in accordance with known techniques. After this is done various other layers as specified may be placed upon it, also in accordance with known techniques.

Decals constructed in accordance with this invention are considered to be much more desirable from a commercial and utilitarian standpoint than prior related devices. Because of the nature of the polyamide surfaces used with this invention these surfaces and the bonds achieved upon them are of an essentially temperature stable character. Hence, the dry transfer decals herein described operate satisfactorily over the entire range of normally encountered temperatures. Further, the release obtained with these decals is substantially unaffected by ambient moisture and various other environmental influences. They may be stored for prolonged periods. Also decals as herein specified are considered very desirable inasmuch as the transfer structures removed from them and placed upon receiving surfaces appear to have a comparatively very smooth, shiny type of surface appearance which is very desirable for many usages. This surface configuration is considered to be a consequence of the surface character of the dry release sheet employed in such decals.

Because of the nature of this invention it is to be considered as being limited only by the appended claims forming a part of this disclosure.

I claim:

1. A dry release sheet for use in a dry transfer decal which includes a "hard" clay coated, calendered paper, one surface of said paper coated with a polymer mixture having the formula

$$HO\{OC—R—CONHR'—NH\}_nH$$

in which R is a hydrocarbon group of indeterminate configuration derived from linoleic acid and having 34 carbon atoms and in which R' is the group $—CH_2CH_2—$ and n has a value sufficient that said polymer has a melting point of from about 90° to about 115° C. and an amine value of 3, a specific gravity of 0.98, an ash content of 0.05 percent by weight, and a viscosity of from about 7 to about 45 poises at 150° C. as measured by #2 spindle at 20 r.p.m. on a Brookfield viscometer.

2. A dry transfer decal which includes: a dry transfer release sheet consisting of a "hard" clay coated calendered paper sheet, one surface of said paper sheet being uniformly covered with a polymer mixture having the formula

$$HO\{OC—R—CONHR'—NH\}_nH$$

in which R is a hydrocarbon group of intermediate indeterminate configuration derived from linoleic acid having 34 carbon atoms and in which R' is the group $—CH_2CH_2—$ and in which n has a value sufficient that said polymer has a melting point of from about 90° to

about 115° C. and an amine value of 3, a specific gravity of 0.98, an ash content of 0.05 percent by weight and a viscosity of from about 7 to about 45 poises at 150° C. as measured by a #2 spindle at 20 r.p.m. on a Brookfield viscometer; said surface holding a transfer structure, said structure including a polymeric surface layer based on a polymer selected from a group consisting of cellulose esters and ethers, acrylic, vinyl chloride and vinyl acetate polymers, said surface layer being incompatible with said surface on said paper sheet and being polar in character.

3. A dry transfer decal as defined in claim 2 wherein said surface layer is created from a polymer composition having an interfacial surface tension which differs from the interfacial surface tension of said covered surface of said release sheet by less than about 10 dynes per square centimeter.

4. A dry release sheet for use in a dry transfer decal which includes a "hard" clay coated, calendered paper, one surface of said paper coated with a polymer mixture having the formula

$$HO\{OC—R—CONHR'—NH\}_nH$$

in which R is a hydrocarbon group of indeterminate configuration derived from a fatty acid having terminal carboxyl groups and in which R′ is the group $—CH_2CH_2—$ and n has a value sufficient that said polymer is a solid at ambient temperatures.

5. A dry transfer decal which includes: a dry transfer release sheet consisting of a paper sheet, one surface of said paper sheet being uniformly covered with a polymer mixture having the formula

$$HO\{OC—R—CONHR'—NH\}_nH$$

in which R is a hydrocarbon group of intermediate indeterminate configuration derived from a fatty acid having terminal carboxyl groups and in which R′ is the group $—CH_2CH_2—$ and in which n has a value sufficient that said polymer is a solid at ambient temperatures; said surface holding a transfer structure, said structure including a polymeric surface layer based on a polymer selected from a group consisting of cellulose esters and ethers, acrylic, vinyl chloride and vinyl acetate polymers, said surface layer being incompatible with said surface on said paper sheet and being polar in character.

6. A dry transfer decal as defined in claim 5 wherein said surface layer is created from a polymer composition having an interfacial surface tension which differs from the interfacial surface tension of said covered surface of said release sheet by less than about 10 dynes per square centimeter.

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