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(54) **Dye pattern absorption into plastics.**

(57) Method, apparatus and product are provided for absorption of a dye pattern on and below the surface of a plastic article including webs wherein one or more disposed dyes are applied to the surface of the article in a desired pattern. Sufficient subliming energy by application of heat or application of radio frequency waves to the dye deposited or printed surface of the plastic article, sufficient to heat the dyes to a sublimation temperature therefor causes the dyes and dye pattern to sublime on and below the surface of the plastic article.

Also provided is a method for laminating or fusing the reverse side of the plastic article to a substrate during the dye sublimation process.

Also provided is a method for thermoforming the plastic article during or after the dye sublimation process.

Further provided is a decorated plastic article having a substantially non-porous surface penetrated with dispersed dyes therein in a pattern, said pattern being durable against weathering. The article can be of thermoplastic or thermo-set plastic.

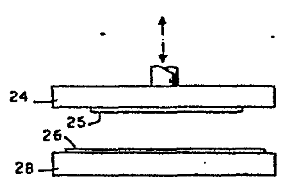

FIG. 3

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Croydon Printing Company Ltd

"DYE PATTERN ABSORPTION INTO PLASTICS"

This invention relates to dye absorption into plastics, particularly dye absorption on, into and below plastic surfaces.

Dye decorating and printing on plastic surfaces has frequently been attempted with varying degrees of success. Surface printing of plastic articles, eg. commercial signs, is done commercially with the drawback that surface printing and decoration is subject to wear and/or chipping and fading after several weeks exposure to the weather including the sun. Attempts have been made to dye decorate and print plastics below the surface thereof with sublimable dyes; see for example USP 3,860,388 to Haigh (1975) and USP 4,059,471 also to Haigh (1977), which patents relate to dye absorption into thermoplastics and thermo-set plastics.

In a previous prior art process for textile or fabric decorating, sublimation dyes are printed on paper, e.g., in patterns, known as heat transfer paper. The heat transfer paper is placed e.g. against drapes or wall paper and heat applied, which causes the dyes to sublime from the heat transfer paper to form clear dye patterns in the drapes or wallpaper (or other fabric). However, if such process is attempted with plastic sheet as the dye receptor surface, upon application of heat and pressure, the heat transfer paper adheres to the heat-softened plastic, since the heat required to sublime the dyes is often sufficient to soften the plastic surface, to the detriment of the end product.

The above prior art patents, however, disclose a solution to the above problem by interposing a polyolefin separator sheet between the heat transfer paper and the dye receptor plastic surface. Heat and pressure are applied as more fully discussed below, which causes the dyes from the heat transfer paper to sublime through the separator sheet and on and into the receptor plastic sheet in a clear pattern. The sheets are then cooled and the transfer paper and separator sheet removed from the receptor plastic sheet and a dye decorated plastic sheet is obtained.

However, while the above prior art process is successful in transferring clear dye patterns on and below plastic surfaces, it requires the preparation of the above heat transfer papers and the positioning of suitable intermediate separator sheets between the heat transfer paper and the plastic receptor surface which accordingly adds steps, delay and expense to obtaining the dye decorated and/or printed plastic end product.

Accordingly there is a need and market for an advance in the dye absorption decorating and printing of plastic products which omits certain of the above process steps, which speeds up the dye absorption process, reduces the cost thereof and even obtains greater clarity and definition of dye decorated products.

There has now been discovered a method for dye absorption decoration of plastic articles wherein a separator sheet is omitted and patterns of dispersed dyes are transferred on and below the surface of a plastic article in clear vivid patterns. Moreover the dyes penetrate below the above plastic surface in greater concentrations than previously possible with an intervening separator sheet, to produce a dye decorated plastic, with wearproof design of improved clarity, definition and intensity.

Broadly the present invention provides a method for transferring a dye pattern on and below the surface of a plastic article comprising applying one or more dispersed dyes in a desired pattern to the surface of the plastic article and applying sufficient subliming energy to such article and the dyes to sublime a substantial portion of the dyes on and below the surface of the plastic article.

In one embodiment of the method of the invention, heat energy is applied to the plastic article to heat such article to sublime the dyes into the plastic as aforesaid.

In another method embodying the invention, radio frequency energy is applied to the plastic article to heat such article sufficiently to sublime the dyes on and below the surface of the plastic article as aforesaid.

In other methods of the invention, the printed dye receptor is laminated or fused to a substrate or issuing extrudate during the dye sublimation process.

In another method of the invention, the printed dye receptor is molded during or after the dye sublimation process.

The invention further provides decorated plastic articles, including molded articles and webs, having a surface penetrated with dispersed dyes in a pattern.

By "subliming energy", as used herein is meant, sufficient energy applied to the dye receptor disclosed herein, to cause such dyes to vaporize or sublime and to cause the dye receptor to become susceptible to penetration by the sublimed dyes.

The invention will become more apparent from the following detailed specification and drawing in which;

Figures 1 and 2 are partial elevation views of apparatus employed in a dye transfer process of the prior art;

Figure 3 is a partial elevation view of a dye printing apparatus employed in the method embodying the present invention;

Figure 4 is a partial elevation view of a dye transfer apparatus employed in the dye transfer method embodying the present invention;

Figure 5 is a partial elevation view of another apparatus employed in the dye transfer method relative to the apparatus of Figure 4;

Figure 6 is a partial elevation view of another apparatus employed in another embodiment of the dye transfer method of the present invention;

Figure 7 is a fragmentary elevation view of another dye transfer method embodying the invention;

Figure 8 is a fragmentary elevation view of a dye penetrated article of the present invention;

Figure 9 is a plan view of a dye pattern absorbed plastic article;

Figures 10 and 11 are schematic elevation views of other dye transfer apparatus employed in the dye transfer methods embodying the present invention;

Figure 12 is a schematic elevation view of another embodiment of the dye transfer method of the present invention;

Figure 13 is a schematic elevation view of another embodiment of the dye transfer method of the present invention;

Figure 14 is a schematic partial elevation view of still another embodiment of the dye transfer method of the invention;

Figures 15 and 16 are partial sectional elevation views of another method embodying the dye transfer method of the invention; and

Figure 17 is an elevation view of a plastic product made by the dye transfer method of the present invention.

Referring in more detail to the drawings, the above prior art patents disclose a method for transferring patterns of dispersed dyes to a plastic dye receptor by interposing a separator sheet between a heat transfer paper and the dye receptor plastic web, as shown or indicated in Figures 1 and 2. Accordingly polyethelene separator sheet 12 is placed between heat transfer paper 10 and dye receptor plastic web 14, between the plates 16 and 18 of the press 20, as shown in Figure 1. The press is closed to press the above sheets together, e.g. at 10 psig and temperatures of over 230° F are applied, which causes the dyes to sublime from the heat transfer paper 10 through the separator sheet 12 and on and into the receptor plastic web 14 in a clearly defined pattern. The sheets are then cooled in place or transferred to a cooling station eg. station 22, shown in Figure 2; the transfer paper 10 and the separator sheet 12 are removed from the receptor plastic web 14 and a decorated plastic with a pattern which penetrates below the surface thereof is obtained.

As noted above, the present invention is an improvement on the above process in that certain of the above steps are omitted and such process is speeded-up. Accordingly, the heat transfer paper is omitted and the printing plate 24, carrying a desired pattern 25 thereon, eg. a photo-image or a raised or grooved image, is coated with selected dispersable dyes (eg. by brush, pad, roller or other means known in the art) and the coated pattern 25 is lowered into direct contact with the surface of a plastic article e.g. plastic receptor sheet 26, on support member 28, as shown in Figure 3 to print the resulting dye pattern on the surface thereof. The plate 24 is then raised above the printed sheet 26. At this point if desired, additional dyes can be added to the same or a different pattern on the plate 24 and the plate can be indexed to print in the same or a different location on the sheet 26, and the plate 24 is again lowered to further print a dye pattern on the surface of the receptor sheet 26.

The so-printed plastic sheet 26 is then advantageously placed between a pair of inert release sheets 34 and 36, which sheets are then placed between the plates 30 and 32 of the heating press 33, as shown in Figure 4. The release sheets 34 and 36 are of inert material eg., polytetrafluoroethylene known as teflon, which release sheets serve to confine the vaporized or sublimed dyes and direct them into the receptor sheet 26 for virtually complete dye transfer and absorption into the receptor sheet 26. The release sheets further assist the removal of the dye absorbed receptor sheet 26 from the press 33 after such dye transfer step. The press 33 is closed e.g. by lowering the plate 32 into contact with the upper release sheet 34 of the three sheet assembly 29, which assembly 29 rests on support plate 30, to apply a pressure, of e.g. 30 psig and heat, e.g. at 400° F for about thirty seconds, which causes the dyes to quickly sublime on and into the plastic receptor sheet 26 in a clearly defined pattern. The so-decorated sheet 26 is then either cooled in place or transferred with said release sheets, to a cooling station e.g. cooling press 38, having cooled plates 37 and 39 as shown in Figure 5, which plates desirably close on the three sheet assembly during the cooling step. The plastic is cooled below its softening temperature, e.g. 200° F, the press 38 is opened, the release sheets removed and a decorated plastic product with clearly defined, wear-proof design is obtained, e.g. product 42 having design 44, as shown in Figure 9.

The steps shown in Figures 3, 4, and 5 can take place in about thirty seconds each.

In another embodiment of the method of dye absorption into plastics of the invention, the plastic receptor sheet 26, printed on its surface with dyes as shown and discussed above relative to Figure 3, is placed in a dielectric heater or RF press 40, which emits radio frequency waves which heat a dielectric, ie. the dye receptor sheet 26, to a dye sublimation temperature, as indicated in Figure 6. Accordingly, the receptor sheet 26 is placed between a brass plate 51, above, and a Bakelite pad 53 below, which plate 51 and pad 53 are slightly larger in area than the receptor sheet 26 and the three layers are placed in the RF press 40 between the two electrodes or plates 55 and 57 of such press 40, as shown in Figure 6. The lower plate 57 advantageously has a resilient pad 59 mounted thereon, as shown in Figure 6. The plates are connected by conductors 61 and 63 to a power source of eg 2-90 megahertz (mHz) produced by a high frequency oscillator (not shown). The brass plate 51 serves to uniformly distribute the RF waves through the receptor sheet 26 and the Bakelite pad 53 prevents the RF waves from penetrating and damaging the lower plate 57.

The Bakelite pad is an inert plastic pad of eg polyethylene, ABS or other inert plastic barrier.

Radio frequency signals of about 2 to 90 mHz at about .1 to .5 kw/sq. in. across the area of the sheet are generated for 1 to 12 seconds, which heats up the surface of the plastic receptor sheet 26 to sufficiently heat the dyes to sublime on and below the surface of said receptor again in a clearly defined pattern, as indicated in Figure 6. The so-decorated receptor sheet 26 is then either cooled in-place or transferred e.g., with a cover sheet eg of teflon (not shown) and the Bakelite pad 53, to a cooling station, eg., station 38, shown in Figure 5. The plastic sheet 26 is cooled, as discussed above, to obtain the dye-absorbed plastic product, e.g., product 42 having design 44, shown in Figure 9.

If desired a pair of teflon release sheets (not shown) can be placed above and below the receptor sheet 26, i.e., between said sheet 26 and the brass plate 51 above, and between said sheet 26 and the Bakelite pad 53 below. However, it has been found that the brass plate 51 and the Bakelite pad 53, in flanking the dye receptor sheet 26 serve also to confine the sublimed dyes therebetween in said sheet 26. Further the nature of the RF energy applied to the molecules of the receptor sheet 26, attracts the sublimed dyes into said sheet, markedly reducing the tendency of such sublimed dyes to escape.

It is frequently desired to obtain a dye decorated end product of greater thickness, depending upon the structural requirements of the end product. Accordingly it is advantageous to position a dye printed receptor web atop a substrate web so as to use one heat and pressure step to sublime the dye pattern into the upper web while fusing or laminating the upper web to the substrate or lower web in one step. Accordingly, the dye-printed plastic receptor sheet 26, positioned atop substrate or sublayer plastic sheet 27, are both placed between release sheets 29 and 31 and such sheet assembly is placed, in turn, between the plates 41 and 43 of dye transfer station 39, as shown in Figure 7. The sheet assembly can accordingly be inserted between the plates 30 and 32 of thermo-press 33, shown in Figure 4 or between the plates of radio frequency station 40, shown in Figure 6, the assembly being heated to sublime the dyes into the upper sheet 26 while laminating said sheet 26 to the substrate 27. The so-bonded product with its release sheets 29 and 31, can be either cooled in-place or e.g. between the plates of the cooling station 38 of Figure 5 and the release sheets separated therefrom, to obtain the fused or laminated plastic, dye-absorbed product 45, shown in Figure 8.

In other methods embodying the present invention, at least some of which have continuous dye printing or dye transfer features, a continous sheet of dye receptor plastic 50, issues from a feed roll 52, through the dye-depositing or printing station 54, around a guide roll 56, to a wind up roll 58, as shown in Figure 10. In the dye-depositing station is an ink applying roll 60, in contact with the pattern printing roll 62, which rotates into contact with the dye receptor plastic sheet 50, as it passes through the nip of the pattern roll 62, and the impression roll 64, which forms a pressure nip therewith and assists the transfer of a dye pattern from the pattern roll to the plastic web 50 and the so-printed dye pattern dries on the web, in air or by drying means not shown, en route to wind-up on the roll 58, as indicated in Figure 10.

In a related process, plastic sheet 66 from a stack of such sheets 68 is passed through a printing station 70, dried e.g. in air or at a drying station not shown, and stacked with other printed dye pattern sheets in a stack 72, as shown in Figure 11. The printing station 70 includes one or more dye applying rolls 74 which distributes dyes on a pattern-bearing roll 76, the so-formed dye pattern being transferred to an intermediate or offset roll 78, which prints or deposits the dye pattern on the plastic sheet 66 as it passes through the nip of the offset roll 78 and the co-rotating impression roll 80, as shown in Figure 11.

In another dye transfer process embodying the invention, having an intermittent operation, plastic dye receptor sheet 82, having a dye pattern printed thereon, positioned between teflon release sheets 84 and 86 ride on endless belt 88, between the platens 90 and 92, of a thermal press 94, as shown in Figure 12. The lower platen 92 advantageously is stationary and has a flexible pad 93 covering the major part of its upper surface and both platens 90 and 92 have heating means therein, e.g. electric heating coils, (not shown), for controlling the temperature thereof. The upper platen 90 is raised and lowered against the lower platen, by means not shown, to obtain the desired pressure therebetween, as indicated in Figure 12.

Spaced from the heating press 94, is cooling press 96, having an upper platen 98 and lower platen 100, advantageously surmounted with a surface pad 102, as shown in Figure 12. The upper and lower platens are cooled e.g. by liquid coils mounted therein (not shown) and the upper platen 98 is moveable up and down relative to the stationary lower platen 100, to adjust the pressure therebetween as desired. The endless belt 88 is rotated and stopped as desired, by means not shown, which accordingly moves the printed dye receptor plastic sheet 82 and its release sheets 84 and 86 into and through the heating and cooling stations 94 and 96, as desired.

In operation, the dye receptor plastic sheet 82 and the release sheets 84 and 86 are advanced on the belt between platens 90 and 92 of the heating station 94. One or both of the platens eg the upper platen 90, is heated to the desired temperature eg 350° F, and the upper platen is lowered, compressing the sheets 84, 82 and 86 against the now stationary belt 88, the press distribution pad 93 and the lower platen 92, at e.g. 30 psig, for a desired period, e.g. 30 seconds, after which the platen 90 is raised and the endless belt 88 reactivated to move the plastic sheet 82 and release sheets 84 and 86 into the cooling station 96, between the platens 98 and 100. The belt 88 then stops and the upper platen 98 is lowered into pressure contact with said 3 sheets at a desired pressure, e.g., of 10 psig and cooling liquid at eg 40° F, is circulated through the coils (not shown) of at least the upper platen 98, to cool the dye absorbed plastic sheet for the desired period, e.g. 30 seconds. The platen 98 is raised and the endless belt 88 is activated to advance the 3 sheets out of the cooling station to near the end of the endless belt. The release sheets 84 and 86 are then removed to obtain the dye pattern absorbed plastic sheet 83, as shown or indicated in Figure 12 and the cycle is repeated for successive dye printed plastic sheets.

It will be recognized that the platen 90 of the heating station 94, shown in Figure 12, need not exert pressure on the plastic receptor sheet 82 and the release sheets 84 and 86, provided sufficient heat of sublimation is supplied to the dye printed receptor sheet 82. However, the platen 90 preferably does close on such layers to apply heat and pressure thereto for close uniform thermal contact, a reduced heating period, and shape control of the sheet 82 to effect the dye absorption of the invention. Similiarly the dye-absorbed receptor sheet may passively cool in air or between the platens of the press of the cooling stations, eg cooling station 96, shown in Figure 12, which platens can be open but are preferably closed for a shorter cooling dwell time and shape control of the dye pattern absorbed plastic sheet. Further the heating station 94, shown in Figure 12, can be replaced with a dielectric heater eg radio frequency station 40 shown in Figure 6, in which the endless belt and dye receptor plastic 82 and release sheets 84 and 86 pass between the spaced plates of such RF station 40, as indicated in Figures 6 and 12. Advantageously, the belt and such tri-sheet assembly are stopped and the RF plates closed thereon eg at 30 psig during the RF heating step.

In a more continuous process of the dye transfer method of the present invention, endless belts of teflon 104 and 106 travel between the platens of the heating stage 108 and the cooling stage 110 as shown in Figure 13. The heating station 108 can be a thermal press, such as heating stage 94 described above with respect to Figure 12 or can be a radio frequency transmitter, such as RF station 40 shown in Figure 6. The cooling stage 110 can be a cooling press such as cooling press 96, described above in reference to Figure 12. In this method of the invention, dye pattern printed plastic web 112 issues from a roll 114, in close contact with the nip of the endless belts 104 and 106, as indicated in Figure 13. The dye pattern printed plastic sheet 112 and the endless belts 104 and 106, stop for eg 30 seconds at the heating station 108, where heat or heat and pressure (closed press) are applied to sublime the printed dyes into the plastic web. The heated dye absorbed web and endless teflon belts 104 and 106 are then advanced to the cooling stage 110 between the plates thereof and such web and belts are halted eg. for an additional 30 seconds, to cool (eg by closed press) the dye absorbed plastic web below its softening temperature and to fix the dye pattern on and below the surface of such plastic web. Of course while one segment of such plastic web is being cooled, another web segment, aft thereof, is being subjected to heat and dye absorption therein, in a production sequence, as indicated in Figure 13. The cooled and dye pattern absorbed web 113 is then advanced to wind-up on wind-up roll 115, as shown in Figure 13.

As discussed above with respect to Figure 7, a substrate of the same or different material can be positioned between the dye pattern printed plastic sheet 82 and release sheet 86 and processed accordingly, as indicated in Figures 7 and 12, to obtain a laminated or fused dye pattern absorbed product, eg product 45, shown in Figure 8. Accordingly the heat of dye sublimation will be also employed for lamination or fusing of the dye receptor plastic sheet and its substrate.

In like manner, a substrate web 116 issuing from roll 118, can contact the bottom surface of the dye receptor web 112 and be laminated or fused thereto in the heating station 108, as indicated, in phantom, in Figure 13, to obtain a thickened, dye-absorbed product.

In yet another process embodying the method of the invention, thermoplastic extrudate 120 issues from extruder dye 122, around a bonding drum 124, as shown in Figure 14. Concurrently, a roll of dye pattern printed plastic web 126, the printed side down, issues from the feed roll 128 and into contact with the hot extrudate 120, between the nip of drum 124 and the endless teflon belt 130, as shown in Figure 14. The heat emitted by the extrudate 120 in contact with the dye printed plastic web 126 is sufficient to effect bonding thereto and sublimation and absorption of the dye pattern into the plastic web 126. The fused or laminated dye pattern absorbed web 132 is passed through the cooling stage 134, eg similar to cooling stage 96, shown in Figure 12, and the cooled dye pattern absorbed plastic web including the substrate web laminated or fused thereto ie web 132, printed side down, passes to wind up, around take-up roll 136, as shown in Figure 14.

In still another embodiment of the method of the invention, dye pattern printed plastic sheet is dye absorbed and thermoformed. Accordingly dye pattern printed plastic sheet 140 is positioned by clamps 142 and 144 over vacuum-forming mold 146, having vacuum ducts 148, as shown in Figure 15. An oven 150, having housing 152 and heater coils 154, 156 and 158, is lowered over the dye printed plastic sheet 140 and the vacuum mold 146, as shown in Figure 15. The heater coils are turned on, sufficient heat is applied to the printed plastic sheet 140 to soften or nearly soften the same, causing the printed dyes thereon to sublime into such sheet. Concurrently, vacuum is applied to the vacuum mold 146 through the vacuum ports 148, by means not shown, which draws the heated and dye pattern absorbed plastic sheet 140, over and around the mold 146, in close conformity therewith, as shown in

Figure 16. The heater housing 150 is raised, the formed and dye pattern decorated plastic article 160 is cooled, the vacuum pump is turned off and the article 160 is removed from the vacuum mold 146 as a dye pattern absorbed and molded plastic article 160, as shown in Figure 17.

Accordingly, the dye receptor can be thermo formed during the dye sublimation step or after the dye sublimation step. Also a previously dye pattern absorbed article can be later reheated and thermoformed including vacuum or pressure formed into a dye pattern aborbed and formed plastic article.

Accordingly the methods of the present invention provide several processes for dye pattern absorption into plastic articles including webs and sheets as well as molded plastic articles.

The dye pattern absorption method of the invention is readily employed with thermoplastic articles eg polystyrene and vinyl sheets and further applies to thermo-set plastic articles, eg polyester sheets and fiberglass sheets. The heat applied to the dye pattern printed plastic article or web, sufficient to sublime the dyes thereon is also sufficient to render the surface of the plastic web receptive to dye penetration to a depth of 10 mils or more. Further data on dye pattern absorption into thermoplastic sheets and thermo-set plastic sheets is provided in Table I hereinafter.

Accordingly, the dye absorption method into plastics of the present invention eliminates certain steps and materials as noted above and includes the following novel steps:

1. Direct printing onto the plastic receptor sheet,
2. The elimination of a heat transfer paper and the positioning thereof,
3. The elimination of a separator sheet and the positioning thereof, and
4. Heat is applied for a considerably shorter dwell time e.g. seconds.

Further the decorated plastic product produced by the above methods of the present invention is believed to have deeper colors and sharper definition, even reproducing "brush-strokes" of the original design over decorated products obtained with the above prior art methods. This is because there is no intervening separator sheet to absorb, screen out, deflect or distort even a small portion of the dispersed dyes originally applied e.g. to a heat transfer paper. Accordingly it is believed that a novel decorated product with a pattern absorbed therein with substantially pure vivid dye hues and "brushstroke" definition and clarity of pattern, is obtained by the methods embodying the present invention.

Accordingly, the present invention provides a method for ready and accurate transfer and absorption of dyes in various colors, prints, patterns, and the like, on and below the plastic surface to be decorated, in a novel, relatively low-cost process, to obtain a dyed plastic product of high clarity reproduction. As discussed above, the so-deposited dyes, upon sublimation, penetrate below the surface of the plastic article and are virtually wear-proof.

The dyes employed herein can be various dyes capable of sublimation at 200° F to 500° F or more, including those dyes in use on heat transfer papers for dye transfer in the textile industry. Preferred are medium energy dyes which sublime between about 300° F and 500° F.

In the methods embodying the present invention, the dye receptor can be any material, such as thermoplastics, which will absorb sublimed dyes and fix them in a durable manner. The dye receptor materials suitable for the present invention include: polycarbonates, vinyls, acrylics, polystyrene, A.B.S. (Acrylonitrile - Butadiene-Styrene) and like extrudable polymers as well as thermo-set plastics including polyesters.

The plastic dye receptor can be an article of various shapes, flat, rounded, angular, or a combination thereof, and can be pronounced three dimensional objects e.g., containers, thermoformed or molded products and the like or can be plastic webs including sheets, film and/or coating or other articles which are receptive to penetration by dispersed dyes.

Advantageously, the desired dyes are applied to a printing plate or roll having the desired pattern engraved, embossed or photo-imaged thereon or otherwise placed thereon and the printing plate is contacted with the dye receptor surface, one or more times, to deposit the desired dye pattern thereon.

Further the desired dyes and dye patterns can be deposited on the dye receptor by any suitable means, e.g., by hand, pen, brush, and the like, in preparation for the dye sublimation step of the present invention.

Moreover the dyes can be printed or otherwise deposited on two or more surfaces of a dye receptor e.g. on opposite sides of a plastic web or sheet and subjected to the dye sublimation and cooling steps described above to obtain a dye pattern absorbed article on two sides thereof on the same or different dye patterns.

The dyes can be printed or deposited upon the plastic receptor surface in a range from a fraction of a second to 40 seconds or more, depending upon the complexity of the pattern, the number of dyes, and the number of printing steps employed. The press is desirably aligned or indexed relative to the plastic receptor for accuracy in employing a sequence of printing steps thereon. A suitable time for the above printing step can, for example, be about 30 seconds.

The temperatures necessary to effect dye transfer and absorption in the methods of the present invention have been found to be governed by the temperatures required for dye sublimation of the dyes employed and the temperatures at which the dye receptor surface energy level rises to become susceptible to dye penetration, which can be at or below the softening temperatures therefor. These dye absorption temperatures have been found to be from 200° to 500° F and up, depending upon the above materials employed. A preferred temperature range in thermal dye sublimation and absorption is 350° to 450° F. After the dye absorption step, the materials are cooled below the dye sublimation temperature and the plastic softening temperature, and a dye decorated plastic product is obtained e.g., a vivid and sharply defined pattern and/or printed letters and numbers in a plastic web.

The application of the heating stage and the cooling stage in the dye absorption method of the invention, can each be from a fraction of a second to 2 minutes or more depending on the dye receptor being processed and frequently runs from 20 to 80 seconds.

The pressures applied in the heat transfer step of the dyes into the plastic receptor can be from 0 (i.e. no pressure to 100 psig and up and preferably are from 20 to 60 psig. The pressure in the cooling stage can be from 1 to 80 psig, and preferably are from 5 to 40 psig.

Where the upper ranges of heat and pressure are applied to the dye deposited plastic receptor e.g., at 400° F and 80 psig, the dyes sublime rapidly so as to practically explode and penetrate into the dye receptor to a depth of several mils, as hereinafter discussed.

The dye absorbed plastic receptor is then cooled as stated above, to obtain the dye absorbed product.

In the dye sublimation step in a thermal press, such as shown in Figure 4, the dye receptor is covered by a pair of release sheets 34 and 36 of, e.g., teflon, to confine the dyes to the plastic receptor and further to facilitate the separation of the plastic receptor from the press platen after the dye absorption step, as indicated in Figure 4. The release layer can be of other materials, e.g., silicon.

Where it is desired to laminate or fuse the reverse side of the dye receptor to another material, the lamination as indicated, can be carried out concurrently with the dye absorption step in the above temperature range of 200 to 500° F, depending upon the substrate employed.

In the applied pressures necessary to effect dye transfer and absorption, 0 to 100 psig has been found sufficient. Lamination pressures however run considerably higher, from 30 to 3,000 psig. Employing such pressures, in the method of the present invention, thermal dye absorption and lamination of the plastic receptor to a substrate occurs concurrently. Where the bonded layers are compatable or of the same material they can fuse into one web; where they are different, they bond into a layered laminate web.

The substrates suitable for laminate base material herein include: treated papers, fabrics, plastic materials, including thermoplastics and thermoset plastics, e.g., webs, sheet and film, and any other material bondable to the plastic dye receptor.

In another method embodying the dye absorption process of the present invention, radio frequency waves are applied to the dye deposited plastic receptor, as discussed above, with respect to Figure 6. These RF waves when matched to the dielectric constant of the plastic receptor sheet, couple with the molecules thereof causing oscillitory or rotational motion thereof, which heats up the plastic and thus the dyes printed thereon to a sublimation temperature, causing the dyes to sublime into the plastic receptor web, as discussed above.

The resultant RF heat is generated in the dielectric, the plastic receptor, and in homogeneous materials is a uniform heat, rapidly attained. RF frequencies employed can range from 2 to 90 mHz or more with power output from 1 to 125 kw or more. However to prevent interference with authorized radio communication channels certain known shielding procedures are followed.

While the dielectric constant of air is 1, the dielectric constant of many plastics ranges from 1 1/2 to to 5; eq at 1 mHz for: ABS-polycarbonate alloy 2.4 to 3.8; polycarbonates 2.92 to 2.93; polystyrene 2.4 to 3.8 and PVC 3.3 to 4.5. Accordingly the RF frequency selected depends upon the dielectric constant of the dye receptor plastic and when properly matched therewith, serves to couple with the molecules thereof and raise the temperature of the plastic to a sublimation temperature for the dyes printed thereon.

Accordingly for plastic dye receptors having a dielectric constant from 1 1/2 to 5, radio frequency signals of eg from 1 to 100 mHz at a suitable power, eg 1 to 125 kw, are effective to heat the dye receptor and to transfer the dye pattern from the surface to within the dye receptor web in a rapid and accurate sublimation process, eg in 2 to 12 seconds.

The power of the RF signal varies with the area of the dye receptor, eg for a web 3 x 4 in. (12 sq. in.), 6 kw or .5 kw/sq in. provides effective dye sublimation. For a larger area dye receptor, eg 25 x 38 in. (950 sq. in.) 100 kwatts or slightly less than .1 kw/sq in. provides effective dye sublimation. Accordingly the power requirements of the RF signal appear to diminish per square inch as the area of the dye receptor increases and as indicated herein, has been found to range from about .09 to .5 kw/sq. in. A suitable pressure range in the RF dye sublimation process, eg the press shown in Figure 6, extends from a fraction to 20 psig, eg a suitable pressure is 5 psig and the time for applying such pressure ranges from 1 to 12 seconds or more.

As noted, the dye receptor and accompanying layers are desirably transferred from the RF dye sublimation stage to a cooling stage, eg a cooling press. Such cooling press is desirably closed on the dye receptor itself or in combination with adjacent layers from the RF heating press (per Figure 6) at a pressure of a fraction to 20 psig and a suitable pressure is, eg 5 psig, for 1 to 20 seconds or more. The cooling press is thereafter opened and a dye pattern absorbed plastic article obtained. The cooling of the plastic dye receptor below the dye sublimation temperatures fixes the dyes and dye pattern in the receptor and the release sheets or other adjacent layers (per Figure 6) are then removed therefrom.

Heating and cooling the dye receptor under pressure is desirable since such pressure can prevent unwanted deforming of the dye receptor as it undergoes temperature charges above and then below its softening temperature.

The radio frequency dye-absorbed plastic product can be subsequently laminated to one or more substrates by applying heat and pressure as above described.

In the above dye absorption methods, whether by heated press or by RF heating, it is sufficient if the dye receptor is heated from above, where such receptor is a web 20 mils thick or less. Where such receptor has a thickness of greater than 20 mils, either singly or in combination with a substrate, it is desirable to heat such webs from below as well, e.g., a few degrees below the softening temperature thereof so that such web or webs are evenly heated during the dye sublimation process and/or laminating process and warping of the dye absorbed end-product is avoided. Even in the RF dye sublimation process, for dye receptors over 20 mils thick, it is well to heat the lower plate or support member for the dye receptor web or webs to a few degrees below the softening temperature thereof before and during the dye sublimation process to prevent or minimize warping of the dye absorbed end product.

As previously indicated, the above methods of the invention of heat press thermal dye absorption and radio frequency dye absorption serve to transmit dye patterns intact into thermoplastics and thermo-set plastics. By thermo-set plastics as used herein, is included cross-linked polymers such as polyester webs, including those under the trade name "Mylar", as well as thermocast plastics including cross-linked polymers of e.g. glass fiber impregnated with polyester resin, known as fiberglass. While the methods of the invention produce the unexpected result of transmitting dye patterns of high definition into thermoplastics, e.g., non-cross-linked polymers such as polystyrene and vinyl, it is even more unexpected that such dye patterns could also be transmitted below the surface of cured thermoset plastics.

The dye absorption methods of the present invention permit dyes and dye patterns to be absorbed several mils into and below the surface of a plastic dye receptor. Such depth of dye penetration will depend upon the nature of the dye receptor plastic, its thickness, the nature and amount of the dyes employed, the temperature, pressures, and radio frequencies applied, the duration or length of the dye absorption step and the like. However, according to the methods of the present invention, dye absorption into the various plastic-receptors are regularly obtained from fractions of a mil to 10 mils or more and preferable from 3 to 8 mils, to obtain a highly defined pattern with vivid colors in a wear-proof design.

The following examples are intended to illustrate the methods of the present invention and the products thereof and should not be construed in limitation thereof.

EXAMPLE 1.

A sheet of polystyrene 10 mils thick by 25" x 38" was passed through the nip of an offset printing press, such as shown in Figure 11 and a lithograph roll coated with dispersed dyes of various colors in a pattern, such as shown in Figure 9, contacted such sheet and printed the above pattern thereon in less than 2 seconds. The so-printed sheet was dried in air at room temperature for 2 hours. The so-printed sheet was then placed between a pair of teflon release sheets of slightly larger size and 8 mils thick each and the tri-sheet assembly was placed between the platens of a heating press, e.g., as shown in Figure 12. The press which was heated to 400° F, was closed upon the tri-sheet assembly at a pressure of about 30 psig for about 30 seconds and then opened.

The tri-sheet assembly was then conveyed between the platens of the cooling stage 96, shown in Figure 12. The upper platen, being (liquid coil) cooled to about 50° F, was lowered into a pressure contact of about 5 psig with the tri-sheet assembly on the bottom platen for about 30 seconds. The cooling platen was raised, the tri-sheet assembly was conveyed clear of the cooling press, the release sheets were removed and the plastic web, cooled below its softening temperature, displayed a clear pattern of vivid colors with "brush stroke" definition, absorbed about 6 mils into the polystyrene, in a wear-proof design.

EXAMPLE 2.

The above process was repeated with 10 mil polyester film (Mylar) and a dye penetrated end product was obtained which displayed a clear pattern of vivid colors of high definition, absorbed 7 to 8 mils therein, in a wear-proof design.

EXAMPLE 3.

A sheet of polystyrene of the dimensions of Example 1 and printed accordingly, was placed atop a sheet of compatible ABS of the same dimensions but 70 mils thick and the two layers were placed between 2 teflon release sheets of the size of Example 1. The quadri-sheet assembly was placed between the platens of the heating stage 96, shown in Figure 12, the upper platen 96 was heated to about 400° F and the lower platen was heated to about 280° F, below the softening temperature of the ABS layer and the remainder of the process of Example 1 followed.

Upon removal of the release sheets it was seen that the polystyrene and ABS webs had fused into one continuous integral web, about 80 mils thick, with no discernable strata lines and further that the upper polystyrene portion thereof was penetrated with a clear pattern of vivid colors of high definition, absorbed about 6 mils therein in a wear-proof design.

EXAMPLE 4.

Another 10 mil polystyrene sheet of the dimensions of Example 1 is printed accordingly. The so-printed plastic sheet is placed between a brass plate above and an Bakelite pad below and the tri-layer assembly is placed between the platens of a radio frequency press at about 5 psig, such as shown in Figure 6. The lower press platen is surmounted by a resilient pad also, in the manner shown in Figure 6. The polystyrene sheet is determined to have a dielectric constant of 3.1 and an RF of 27.12 MHz at 100 kw is applied thereto for 5 seconds.

The RF press is opened and the polystyrene sheet with a cover sheet of teflon and the Bakelite pad are transferred to a cooling press such as cooling press 38 shown in Figure 5, the plates are closed thereon, eg, at 5 psig. The polystyrene sheet is cooled below its softening temperature and the sublimation temperature for the dyes. The press is opened and the polystyrene sheet dye receptor separated from the cover sheet and pad, to obtain the plastic sheet with wear-proof design. The dye pattern absorbed polystyrene sheet displays a clearly defined vivid pattern, absorbed 6 to 7 mils into such web and is very similar in appearance and durability with the decorated plastic web made by the process of Example 1.

It has also been found that if the above procedure of Example 4 is repeated with a blank or unprinted dye receptor plastic web in contact with the printed side of a dye pattern printed paper, i.e., a heat transfer paper, that is at least one month old and these two layers are positioned between the brass plate 51 above and the Bakelite pad 53 below, which layers are in turn, positioned between the upper plate 55 and the lower plate 57 of the RF press 40, as indicated in Figure 6, and RF waves are applied as described in Example 4, that after the cooling step above described, a dye pattern absorbed plastic web with depth of pattern of 6 to 7 mils is again obtained. The heat transfer paper separates from the dye decorated product without sticking or adhering to the dye receptor web provided such paper has been aged at least 30 days at room temperature (or higher). If the heat transfer paper has been dye printed within such 30 day period, the dye adhesives and carrier, which hold the dye pattern on the paper, can still be activated in the RF press and adhering of paper to dye receptor occurs.

Accordingly, employing the above aged transfer paper-RF press method, a flexible vinyl sheet ,3" x 4" by 20 mils has been imprinted with a dye pattern on and below the surface thereof. Similarly a fiberglass sheet of polyester resin impregnated in fiber glass matting, 3" x 4" by 31.25 mils (1/32") thick, received a clear dye pattern therein on and below the surface thereof. In each case, the RF waves were transmitted at 27.12 MHz at 6 kw for 5 seconds and the so-heated webs were cooled below dye sublimation temperature in about two minutes.

It has further been found that the above aged heat transfer paper of 30 days or older can only be effectively employed in the above radio frequency dye sublimation process without interleaving a separator sheet, eg of polyethylene. An attempt to use aged heat transfer paper and a dye receptor in a thermal press, eg as shown in Figure 4 results in the adhesion of the heat transfer paper and the dye receptor as previously encountered in the prior art. Accordingly, employing aged heat transfer paper in contact with a blank dye receptor web or article and applying RF dielectric heat, as described above, is another method embodying the present invention for producing dye pattern absorbed plastic articles including webs.

The following table exemplifies dye pattern absorbed and decorated products made by the methods of the present invention as follows:

TABLE I.

DYES	DYE RECEPTOR	THICKNESS	DYE DEPTH
Medium Energy	Polystyrene	10 mils	6-7 mils
" "	Vinyl	10 mils	7-8 mils
" "	Polyester film (Mylar)	10 mils	7-8 mils
" "	Polystyrene-Compatible ABS	10 mils 70 mils	7-8 mils
" "	Vinyl-Polycarbonate	10 mils 125 mils	7-8 mils
" "	Glass fiber impregnated with polyester resin (fiberglass)	62.5 mils	3-4 mils

The above tests were conducted with the dye receptor and its substrate, if any, between a pair of teflon release sheets in a press apparatus similar to that shown in Figure 12, the heating stage operating at about 400° F and 30 psig and the cooling stage operating at about 70° F and about 10 psig, each stage operating between 30 and 40 seconds except for the last two dye receptors wherein the stages operated at about 60 seconds each.

In each of the above tests and in the above examples, a dye pattern absorbed plastic article was produced which displayed a clear pattern of vivid colors of high definition in a wear-proof design.

Samples of the above dye pattern absorbed plastics were exposed for extended periods to ultra violet light and subjected to testing including fadometer tests and were found to exhibit high durability of color retention and pattern definition equivalent to over 2 years in exposure to weather including the sun eg in Florida, Arizona and other states.

Accordingly, the dye pattern absorbed articles of the invention are "durable against weathering" ie. exhibit the above described durability for 6 months or more.

Prior art surface printed outdoor signs show significant weathering, ie, fading, blurring, chipping and wear-off within three months. Thus the dye pattern absorbed articles of the invention include printed and decorated webs highly suitable for use as outdoor surfaces including signs.

CLAIMS:

1. A method for transferring a dye pattern on and below the surface of a plastic article comprising, applying at least one dispersed dye in a desired pattern to the surface of said plastic article, applying sufficient subliming energy to said article and said dye to sublime a substantial portion of said dye on and below the surface of said article.

2. The method of claim 1 wherein said energy is applied by heating the surface of said article and said dye, to a sublimation temperature for said dye, maintaining said temperature until a substantial portion of said dyes have sublimed into the surface of said article and cooling said surface below the sublimation temperature of said dyes and the softening temperature thereof to obtain a dye pattern absorbed plastic article.

3. The method of claim 1 wherein said sublimation energy is radio frequency waves applied to of said article at sufficient frequency and power to heat said article sufficiently to sublime said dyes on and below the surface of said article.

4. The method of claim 1 wherein said dyes are applied to a printing member and said printing member is contacted with said surface to print said dyes on said surface.

5. The method of claim 1 wherein said dyes are applied directly to said surface.

6. The method of claim 2 wherein said surface and said dyes are heated between 330° F and 450° F to sublime said dyes.

7. The method of claim 2 wherein said article is heated between a pair of release sheets which are between the platens of a thermal press at a pressure between 1 to 100 psig.

8. The method of claim 1 or 7 wherein said plastic article is substantially of thermoplastic.

9. The method of claim 2 or 7 wherein said plastic article is substantially of thermo-set plastic.

10. The method of claim 9 wherein said thermo-set plastic is in contact with fibrous carrier material.

11. The method of claim 1 wherein said article is a plastic web, and passing said web through a dye printing stage, a dye subliming stage, and a cooling stage, to obtain a dye pattern absorbed, decorated, plastic web.

12. The method of claim 11 wherein the dwell time in the dye subliming stage and the cooling stage is between 20 to 70 seconds.

13. A method for dye pattern transfer on and below the surface of a plastic article comprising; applying at least one sublimable dye to a printing member in a pattern, contacting said printing member with said plastic article to print said dyes on said article in a pattern and applying sufficient subliming energy to said article to sublime said dyes into said plastic article.

14. The method of claim 13 wherein said energy is heat applied to said plastic article to sublime said dyes into said article and cooling said article below the sublimation temperature of said dyes.

15. The method of claim 13 wherein said energy is a transmission of radio frequency waves applied to said plastic article at 1 to 100 mHz and .09 to .5 kw per sq. in. of the dye presented surface of said article.

16. The method of claim 2 or 7 wherein a dispersed dye pattern is printed on at least two surfaces of said plastic article, which surfaces are heated to sublime the dye patterns into each said surface and cooling said surfaces below the sublimation temperatures of said dyes and the softening temperature of the plastic article to obtain a plastic article with absorbed dye patterns on a least said two surfaces.

17. The method of claim 16 wherein said surfaces are opposite sides of a plastic web.

18. The method of claim 1, 2 or 7 wherein a sublayer of plastic web is placed in contact with the underside of said article and sufficient heat and pressure are applied above and below the multi-plied article to sublime said dyes into the adjacent surface of said article and to laminate or fuse said

plies together and cooling the so-formed article below the softening temperature thereof to obtain a dye pattern absorbed plastic article.

19. A method for transfering a dye pattern on and below the surface of a plastic web comprising printing a dye pattern on the surface of a plastic sheet, contacting the so-printed plastic sheet on the reverse side thereof with an extruded thermoplastic web while said web is sufficiently hot to sublime said dyes and until said dyes sublime into at least said sheet and cooling said sheet and web below the softening temperature thereof to obtain a dye pattern absorbed laminated or fused web.

20. The method of claim 19 wherein said plastic sheet contacts the extruded plastic web in the pressured nip of cooperating rollers and a release sheet is positioned between the dye printed side of said plastic sheet and the adjacent nip roller.

21. The method of claim 1 wherein said dye pattern absorbed article is brought to a sufficient thermoforming termperature and thermoformed into a desired shape to obtain a dye pattern absorbed and shaped plastic article.

22. A method for transfering a dye pattern on and below the surface of a plastic article comprising applying dispersed dyes in a pattern to the surface of a plastic web, applying sufficient heat to said web to prepare it for thermoforming and for subliming said dyes into said web and thermoforming said web into said dye pattern absorbed plastic article.

23. The method of claim 22 wherein said article is formed by vacuum forming said web.

24. The method of claim 22 wherein said article is formed during the dye sublimation step or after the dye sublimation step.

25. A decorated plastic article comprising a substantially non-porous surface penetrated with dispersed dyes therein in a pattern, said pattern being durable against weathering.

26. The decorated plastic article of claim 25 wherein said pattern has high definition of brush-stroke clarity and is durable against the weather for over 1 year.

27. The article of claim 25 being of thermoplastic.

28. The article of claim 25 being of thermo-set plastic.

29. The article of claim 25 wherein said article is a web laminated or fused on its reverse side to a support member.

30. The article of claim 25 wherein said article is a web having two opposed sides and each of said sides has a surface penetrated with dispersed dyes in a pattern so as to be dye penetrated on at least two sides.

31. The article of claim 25 laminated or fused to a sublayer.

32. The article of claim 25 being deformed or molded into a three-dimensional article.

33. An apparatus for transferring dye patterns on and below the surface of plastic articles comprising, means for printing a dye pattern on the surface of a plastic article, means for applying sufficient subliming energy to sublime said dyes on and below the surface of said plastic article to obtain a dye-decorated plastic article.

34. The apparatus of claim 33 wherein the subliming energy means is a radio frequency generating press.

35. The apparatus of claim 33 wherein said article is a plastic web, said printing means a printing press, the subliming energy means is a heated press, which press is opened after the dye transfer step, to permit cooling of the dye-absorbed web.

36. The apparatus of claim 35 having a cooling press and means to convey said web from the heated press to the cooling press.

37. A method for dye pattern transfer on and below the surface of a plastic article comprising, contacting the printed side of aged heat transfer paper having sublimable dyes thereon in a pattern, with the surface of said article, applying radio frequency waves at sufficient frequency and power to said

plastic article to sufficiently heat said article and said surface to sublime said dye pattern on and below said surface, cooling said surface below the sublimation temperature for said dyes and separating the heat transfer paper from said surface to obtain a dye pattern absorbed plastic article.

38. The method of claim 37 wherein said article is a plastic web, said web and said heat transfer paper are placed face-to-face between a brass plate above and an inert barrier pad below, to form a quadri-layer assembly, which assembly is placed between the plates of an RF press, said RF press is closed on said assembly at 1 to 20 psig, RF transmission is applied to said assembly for 1 to 12 seconds, said RF press is opened and the assembly minus the brass plate plus an inert cover sheet is transmitted to a cooling press, said cooling press is closed on said assembly at 1 to 20 psig, to cool said web below the dye sublimation temperature, said cooling press is opened and the respective layers of the assembly are separated to obtain a dye pattern absorbed plastic web.

39. The method of claim 38 wherein a dye pattern is printed directly on said plastic web, said heat transfer paper is omitted and the process repeated.

40. The method of claim 7 wherein said thermal press is opened and said article and said adjacent release sheets are conveyed between the platens of a cooling press, said cooling press is closed thereon to a pressure of 1 to 20 psig to cool said article and said cooling press is opened.

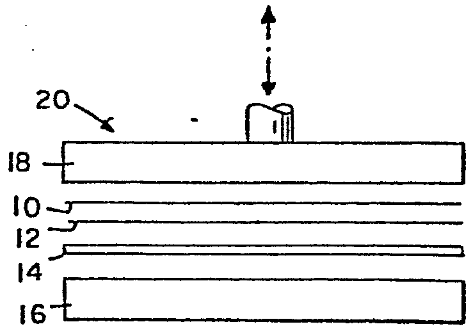

FIG.1

PRIOR ART

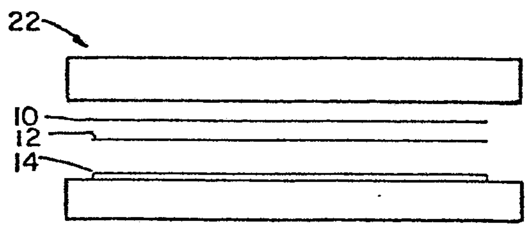

FIG.2

PRIOR ART

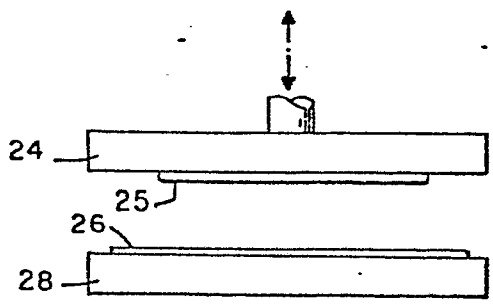

FIG.3

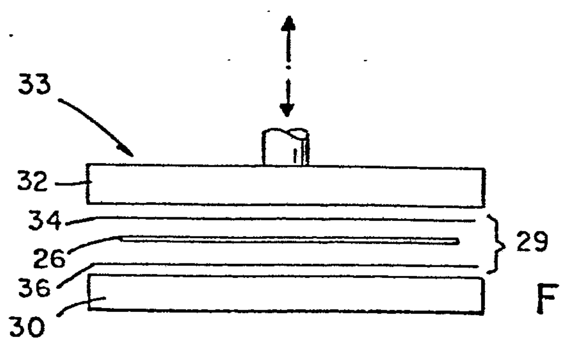

FIG. 4

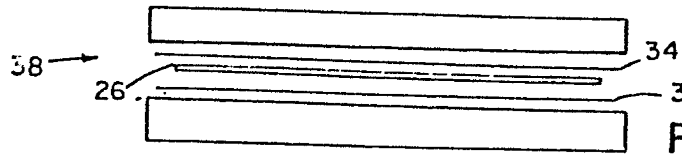

FIG.5

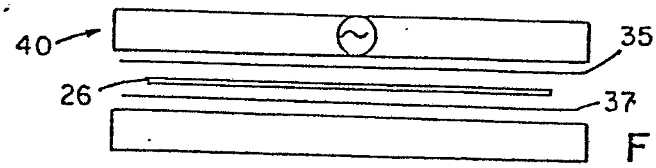

FIG.6

FIG. 7

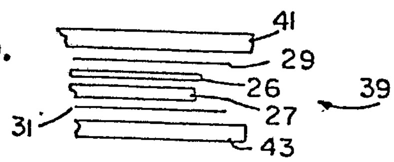

FIG.8

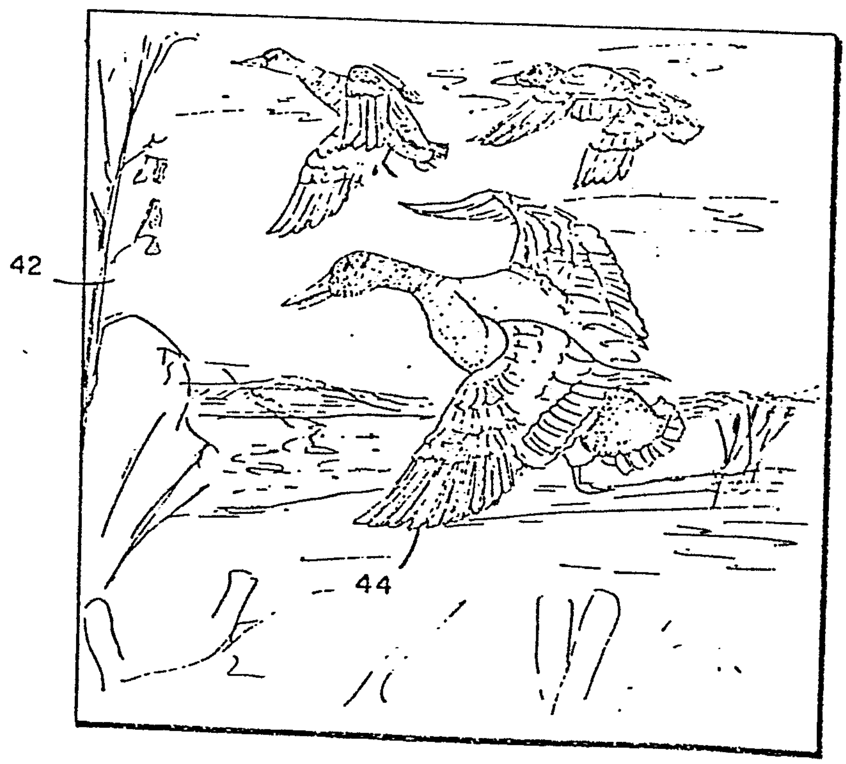

FIG.9

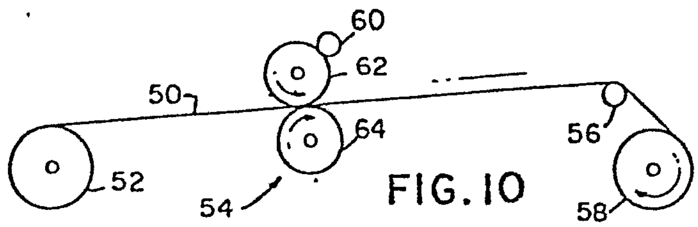

FIG. 10

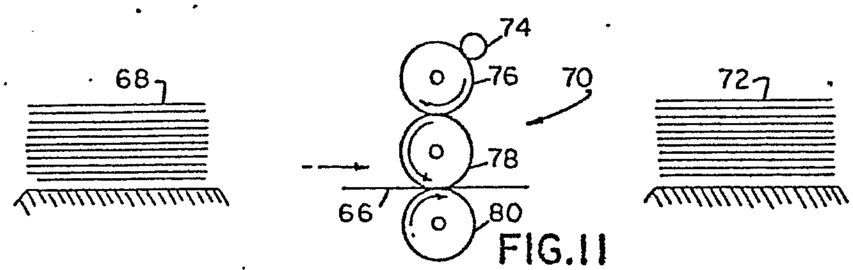

FIG. 11

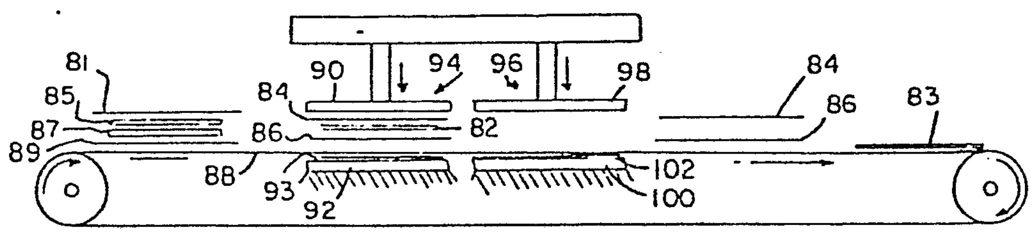

FIG. 12

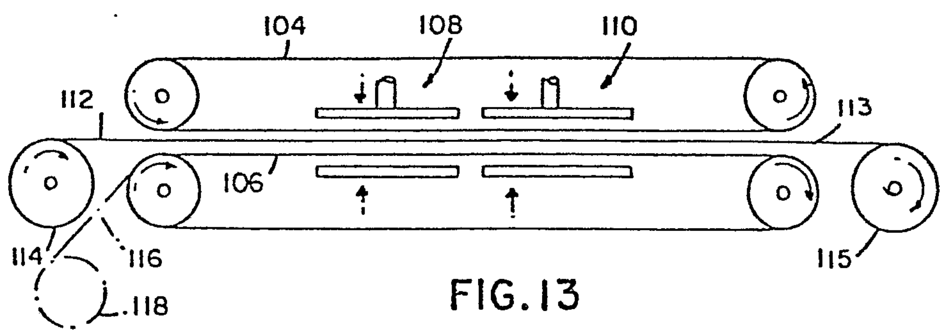

FIG. 13

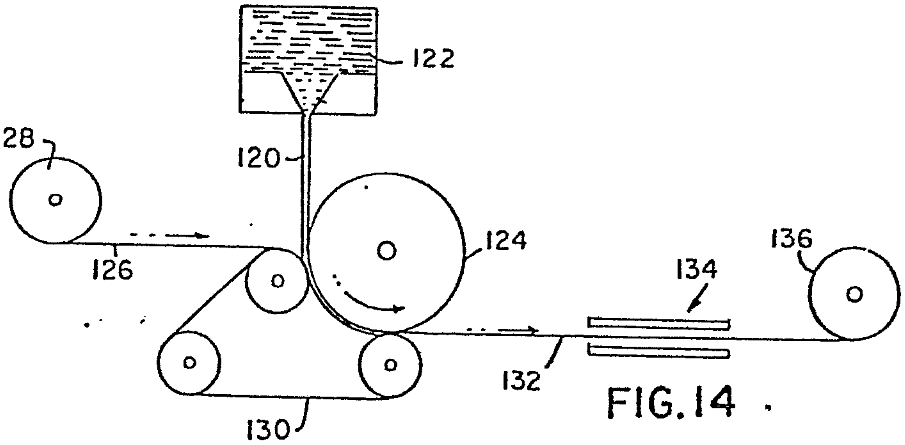

FIG.14

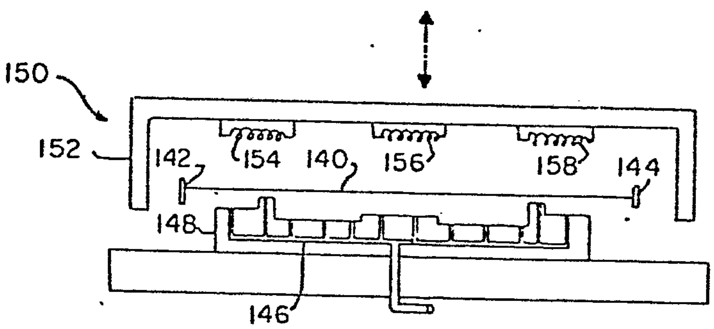

FIG.15

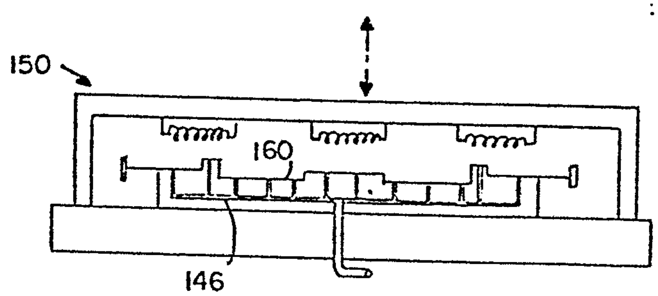

FIG.16

FIG.17