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Continuation of Ser. No. 455,936, May 14,
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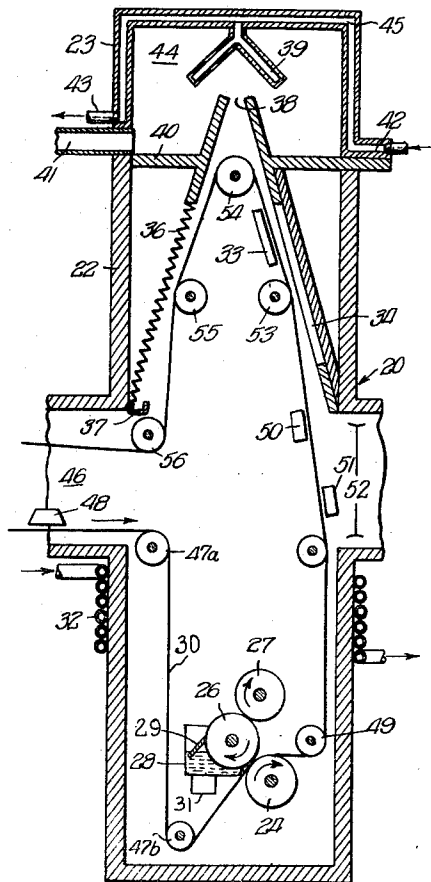
[54] **PRINTING AND COATING APPARATUS**
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118/61, 118/65, 118/325
[51] Int. Cl. **B05c 11/16**
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642, 643, 57, 56, 64 (Wax Digest), 325; 134/122,
64; 117/93.1, 235, 93, 31; 34/4, (Sonic Digest)

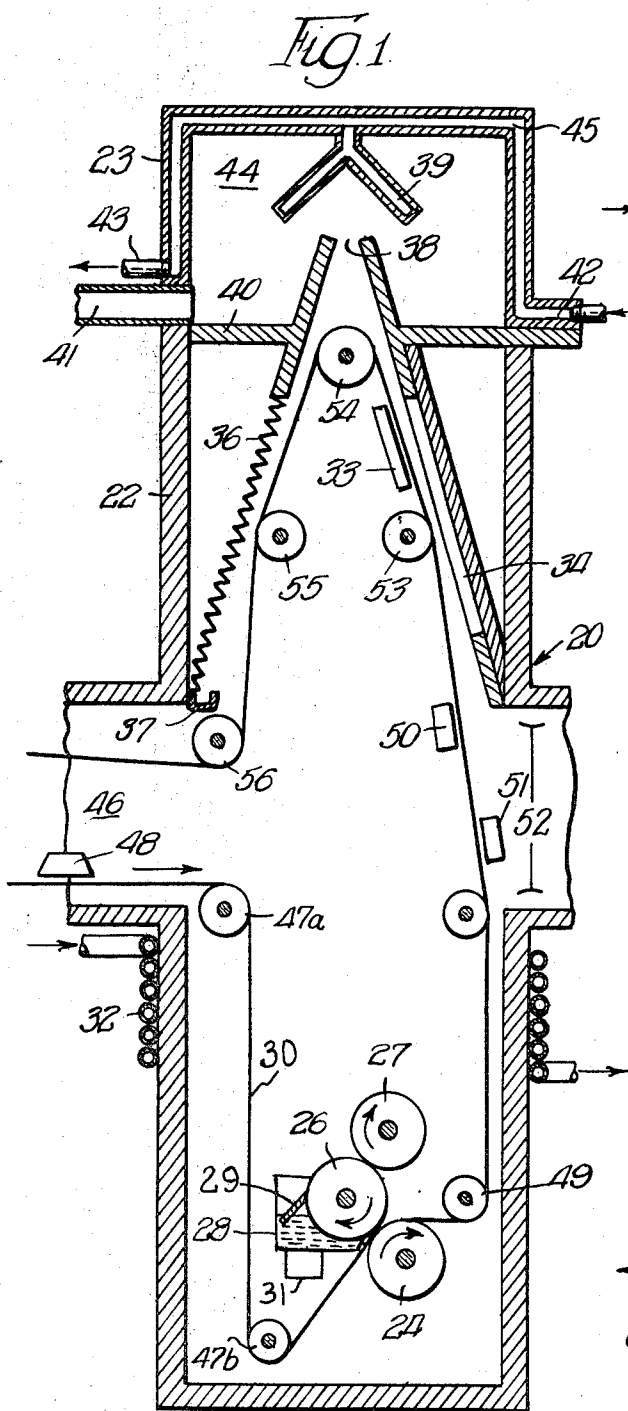
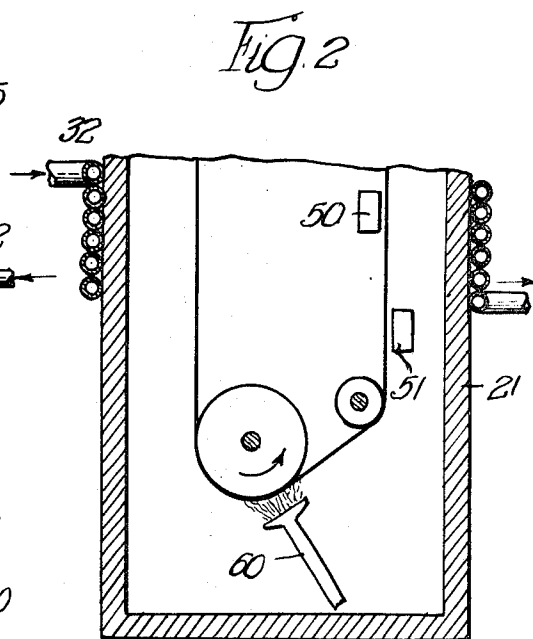
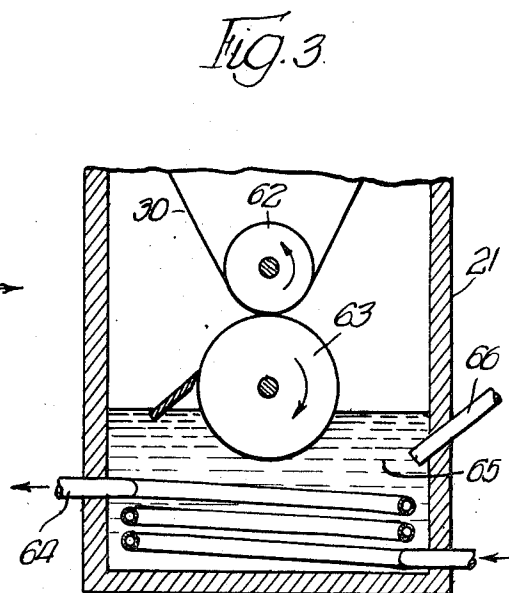
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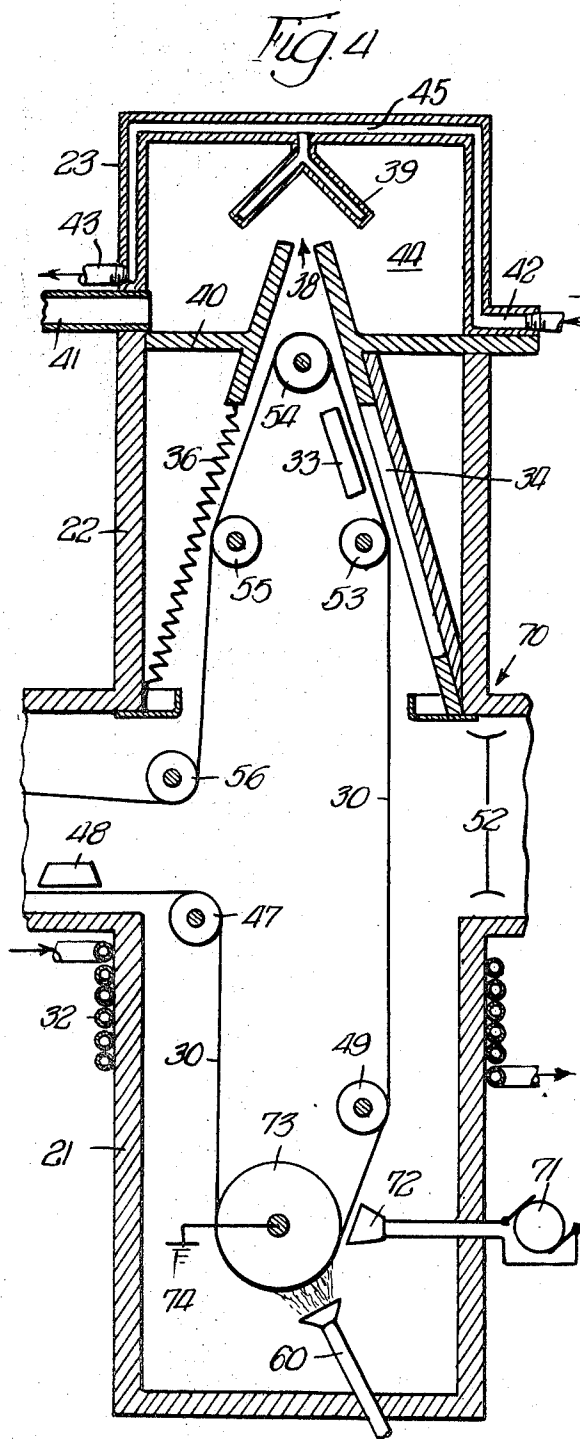
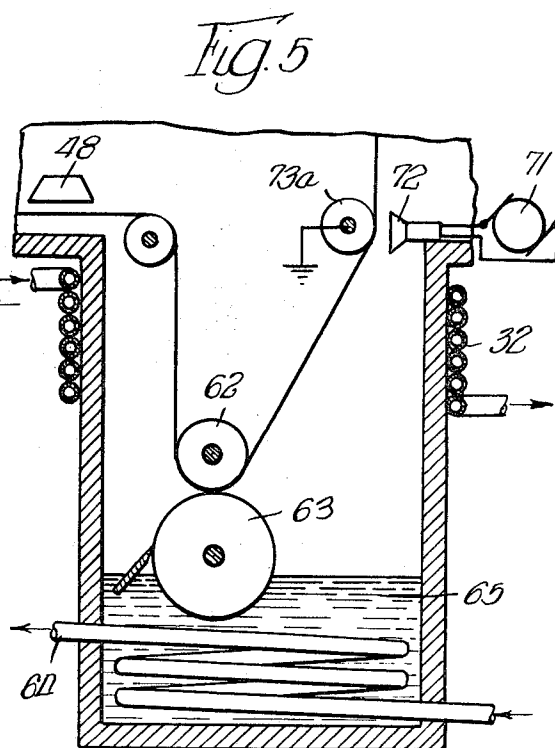
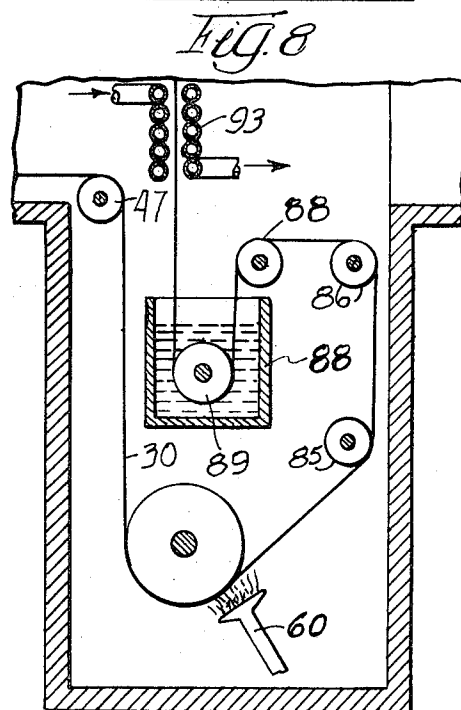
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ABSTRACT: An apparatus for coating web and object surfaces wherein a formulation including a coating component dispersed in a solvent vehicle is deposited onto the web or object surface which is then subjected to improved solvent release means for facilitating vaporization of the solvent constituent in the formulation and/or polymerization and cross-linking within the coating component while on the web or object surface.

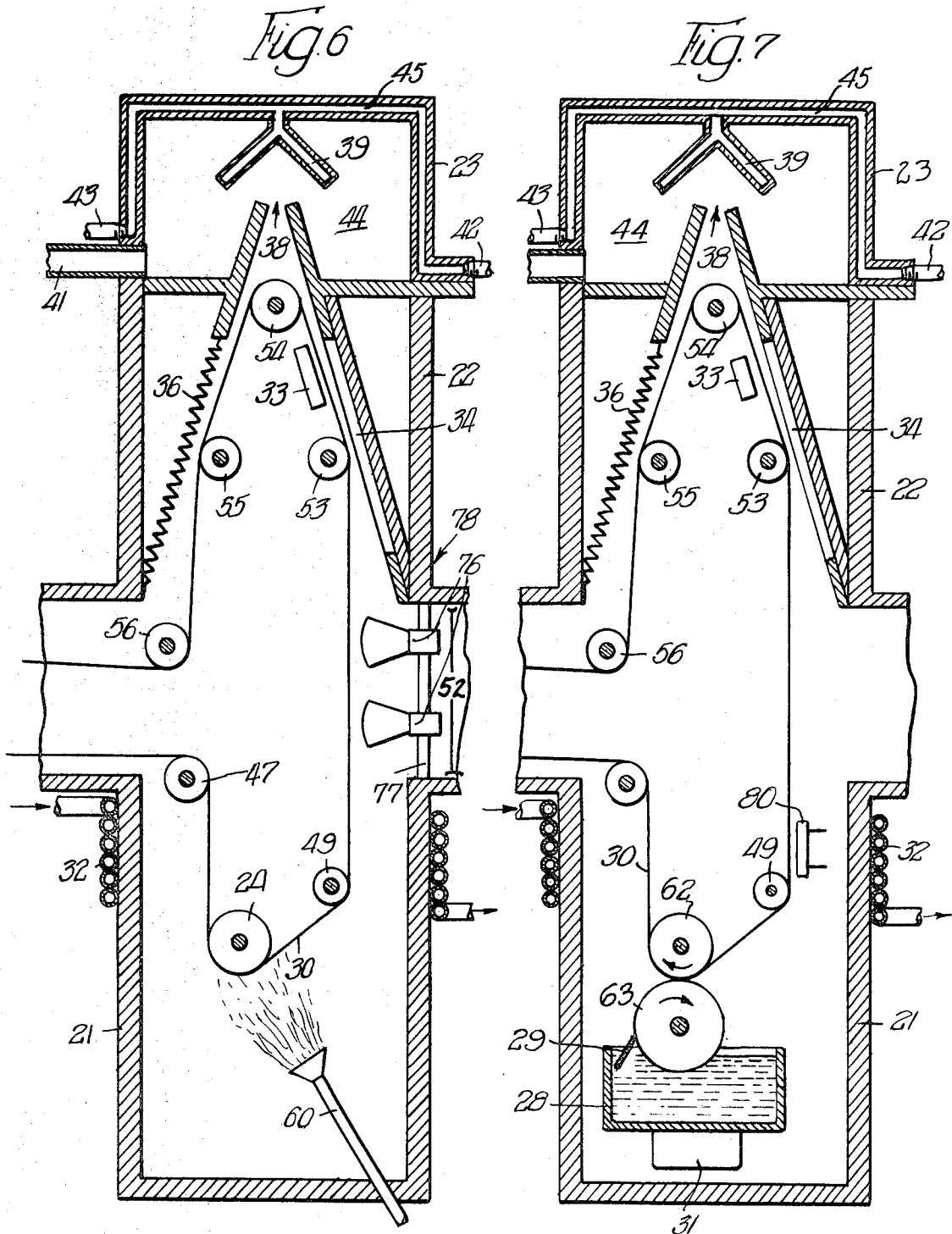




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PRINTING AND COATING APPARATUS

This application is a continuation of Ser. No. 455,936 filed May 14, 1965 now abandoned.

The present invention relates to printing and coating apparatus. More particularly, this invention is concerned with improvements and innovations in apparatus for continuously printing or coating in a nonflammable atmosphere a traveling web or object surface by depositing thereon a suitable ink or coating composition dispersed or dissolved in a heavy solvent vehicle followed by inline treating of the web or object surface with means for effecting improved solvent release and/or bonding of the ink or coating composition to the substrate surface of the web or object surface.

By the apparatus of the present invention, it is possible to accomplish high-speed coating and printing of paper, plastic films, metal foils, textile fabrics, netting, nonwoven fabrics, wires, filaments, fibers and threads. In addition, the method and apparatus of the present invention can also be used for coating of objects such as bottles, cans and the like. The ink or coating composition carried by the heavy solvent vehicle can be deposited onto the substrate surface by any number of conventional techniques which include rotogravure, offset gravure, reverse-roll coating, air-knife, dip coating, kiss roll, floating-knife coating and the like. It has also been discovered that pressurized spraying of liquid in the form of droplets or foam coatings can be advantageously employed in particular coating operations.

According to the present invention the various printing and coating processes referred to above are cooperatively combined with certain expedited solvent release and/or ink and coating composition bonding or polymerizing techniques. While the various embodiments of the invention will be more fully described below, they generally consist of subjecting the printed or coated web to ultrasonic wave transmission, corona discharge, and/or ultraviolet photopolymerization. As used in this application, the term "corona discharge" is intended to include the process of treating a web or object surface with a high-voltage electrical discharge which promotes the advantageous cross linking, polymerization and/or improved bonding of printing and coating deposits on the web or object surface.

A significant aspect of the apparatus of the present invention is that it permits high-speed, low-temperature printing and coating of web and substrate surfaces. Besides offering important advantages by reason of its high-speed coating and printing, the apparatus of the present invention is particularly attractive commercially since it enables substantially complete recovery of the heavy solvent. These heavy solvents include various chlorinated and fluorinated solvents which will be more fully described below.

It is, therefore, an important object of the present invention to provide an improved apparatus for continuously printing or coating a web or object surface by first depositing thereon a suitable ink or coating composition dispersed or dissolved as a monomer or polymer in a heavy solvent followed by immediately subjecting the thus deposited web to means for substantially improving the release characteristics of the solvent and/or the bonding or polymerization of the ink or coating deposit.

Another object of the present invention is to provide low-temperature printing and coating of a web or object surface by first depositing thereon a suitable ink or coating composition dissolved as a monomer or polymer in a heavy solvent vehicle followed by immediately subjecting the thus deposited web to means for substantially improving the release characteristics of the solvent and/or bonding or polymerization of the ink or coating deposit.

Another object of the present invention is to provide apparatus for continuously printing or coating a web or object surface in a nonflammable atmosphere.

Another object of the present invention is to provide an improved web coating apparatus equipped with a unique solvent recovery hood adapted to enable substantially complete solvent recovery in high-speed printing and coating operations.

Another object of the present invention is to provide an improved apparatus for continuously coating a fast traveling web by the pressurized spraying of a coating material dispersed or dissolved in a heavy solvent onto the web.

Another object of the present invention is to provide an improved apparatus for printing or coating a web or object surface by depositing thereon a suitable ink or coating composition dispersed or dissolved in a heavy solvent followed by immediately subjecting the web to ultrasonic sound waves to substantially improve the release characteristics of the solvent for facilitating evaporation thereof.

Another object of the present invention is to provide apparatus for printing or coating a web or object surface by depositing thereon a suitable ink or coating composition which includes a polymerizable component and then subjecting the web to polymerization promotion means for effecting cross linking within the deposited ink or coating to change the characteristics of the coating.

Another object of the present invention is to provide apparatus for converting a web or object surface coating having hydrophillic characteristics to an oleophillic coating through ultraviolet treatment of said coating.

Another object of the present invention is to provide an improved apparatus for coating a web or object surface by first applying a coating material containing a polymerizable component onto the web or object surface followed by inline treatment of said coated web or object surface with polymerization means for directly converting the vapor product absorbed on the web into a plastic coating.

Another object of the present invention is to provide an improved apparatus for printing or coating of a web or object surface by depositing thereon a suitable ink or coating material containing a photopolymerizable component and immediately subjecting the web or object surface to inline treatment with radiation means for promoting polymerization within the deposited ink or coating material.

Another object of the present invention is to provide an improved apparatus for printing or coating a web or object surface by depositing a suitable ink or coating composition carried by a heavy solvent vehicle and then immediately subjecting the thus deposited web or object surface to corona discharge treatment for promoting bonding of the deposited material to the web or object surface and/or changing the physical or chemical characteristics of the coating.

Another object of the present invention is to provide an improved apparatus for printing or coating a web or object surface with ink or coating compositions which include a photopolymerizable constituent by first depositing the ink or coating composition on the web or object surface and then immediately subjecting the deposited coating to ultraviolet rays for promoting cross linking within the coating and bonding thereof to the web or object surface.

Another object of the present invention is to provide an improved apparatus for high-speed coating of a web by depositing thereon at low temperatures a coating composition containing an iron oxide component dispersed in a fluorinated or chlorinated solvent and then subjecting the thus deposited web to a magnetic field prior to evaporation of the solvent so that predetermined particle alignment can be easily obtained thereby.

Another object of the present invention is to provide an improved apparatus for high-speed printing or coating of a fast moving web by providing ultrasonic sound-transmitting means to effect uniform distribution of the ink or coating composition in the solvent vehicle so as to enable uniform application of the ink or coating to the web.

Another object of the present invention is to provide apparatus for coating a web surface with an improved polymeric composition by depositing on the web surface a coating composition dispersed in a nonflammable heavy solvent vehicle and simultaneously at low temperatures subjecting the thus deposited web to a magnetic field and corona discharge treatment.

Other and further objects of the present invention will be apparent from the following detailed description of the accompanying drawings wherein:

FIG. 1 is a schematic view illustrating one embodiment of the apparatus of the present invention wherein ultrasonic wave treatment is employed in combination with three-roll reverse coating of a moving web;

FIG. 2 is a fragmentary schematic view of the lower end of a condenser unit such as illustrated in FIG. 1 modified for aerosol or foam spraying of the web;

FIG. 3 is a fragmentary schematic view such as shown in FIG. 2 illustrating the lower end of the condenser unit of FIG. 1 which has been modified for rotogravure printing or coating of the web;

FIG. 4 is a schematic view illustrating another embodiment of the invention wherein corona discharge treatment is employed in combination with aerosol or foam spraying of a moving web;

FIG. 5 is a fragmentary schematic view of the lower end of a condenser unit of the type illustrated in FIG. 4 but modified for rotogravure printing or coating of the web;

FIG. 6 is a schematic view illustrating a third embodiment of the present invention wherein ultraviolet photopolymerization means is employed in combination with pressurized liquid or foam spraying of a moving web;

FIG. 7 is a schematic view of an apparatus embodying principles of the present invention which is particularly adapted for coating a moving web with magnetic oxide particles and aligning these particles while on the web prior to solvent removal therefrom; and

FIG. 8 is a schematic view of the lower end of a condenser unit embodying principles of the present invention and modified for hot metal drying of a printed or coated web substrate.

Referring to the drawings, and with particular reference to FIG. 1, the numeral 20 generally designates a three-roll reverse coating unit constructed in accordance with one aspect of the present invention. As is shown, coating unit 20 includes a lower shell 21, an intermediate shell portion 22 and a hood 23 which is equipped to collect and condense the evaporated solvent.

The coating depositing component of unit 20 is of the three-roll reverse design and includes an impression roller 24, an application roller 26 and a reverse roller 27. Application roller 26 is positioned so that in rotating it picks up the coating formulation to be deposited from open tank or fountain 28. A doctor blade or knife 29 is arranged to control or meter the amount of coating formulation picked up by application roller 26. Reverse roller 27, having a wiping action on application roller 26, removes the excess coating formulation from application roller 26 and is adjustable for controlling the thickness of the coating deposit and also acts to insure that web 30 receives a smooth and uniform coating layer. Uniformity of the applied coating formulation picked up by roller 26 is provided for by means of a high-frequency impulse generator 31 positioned on the bottom of fountain 28. In this capacity, ultrasonic generators such as those commercially available for The Bendix Company (Davenport, Iowa) and Multisonic Corporation (Westbury, N.Y.) can be advantageously employed. The high-frequency generator unit 31 includes a transducer for converting the high-frequency electrical energy from the generator to ultrasonic waves which, in turn, subject the coating formulation in fountain 28 to high-frequency energy which acts to maintain complete and uniform distribution of the coating material in the fluorinated or chlorinated solvent vehicle.

A coil 32, fitted around the shell portion 21, provides temperature control means to the coating apparatus. For example, in low-temperature coating operations such as are discussed below in reference to FIG. 7, coil 32 can be used to chill or cool the shell zone adjacent to where the web is coated. Similarly, where very heavy coatings are applied to web 30 it may be desirable to send a heated fluid through coil 32 in

order to facilitate evaporation of the solvent vehicle. In this regard, it will of course be appreciated that coil 32 can be sized in accordance with the particular cooling or heating requirements of the coating operation. To the same effect, rollers 24 and 26 may be electrically heated in a well-known manner by any of several commercially available electrical heater units in order to hasten evaporation of the solvent.

Shell portion 22 is equipped with heating elements for effecting evaporation of the solvent vehicle which is absorbed by the traveling web. These heaters will vary in accordance with the web material and coating formulation employed. For example, when coating webs which have a porous texture, it is desirable to position the heating element 33 on the back or uncoated surface of the web 30 so that the solvent vehicle is not driven through the web. On the other hand, when coating non-porous webs, such as metal foils, the heating element 34 is advantageously positioned on the coated side of the traveling web 30. In some operations it is desirable to simultaneously heat both sides of the traveling web 30.

A condenser 36 on the return side of shell portion 22 acts to condense the solvent vapors evolved from the fountain or bath 28 and web 30. At the lower end of condenser 36, a solvent-collecting trough 37 picks up the liquidified solvent and returns it to a storage vessel (not shown) where it is mixed with makeup quantities of coating material and returned to fountain 28 for reuse. Condenser 36 can be advantageously constructed with a corrugated wall for providing additional cooling surface as is disclosed in my U.S. Pat. No. 3,067,056, entitled "Improvements in Printing with Ink Compositions Having Volatile Solvents."

In accordance with an important aspect of the present invention, hood 23 is equipped with a central opening therein through which the evaporated solvent passes. Directly above opening 38 is a Y-shaped baffle 39 on which the vapors condense and run down onto an annular platform 40 for passage through conduit 41 to the storage chamber referred to above in connection with trough 37. Hood 23 and baffle 39 are preferably of a jacket construction with hood 23 being equipped with an inlet 42 and outlet 43 in order to permit the passage of cold water through inner chamber 45 so as to facilitate solvent condensation. In order to improve solvent recovery it is also desirable to communicate the interior chamber 44 of hood 23 with a vacuum pump or other pressure-reducing means.

As is shown in the embodiment illustrated in FIG. 1, web 30 enters coating unit 10 through an opening 46 and is directed around freely rotatable guide rollers 47a and 47b down and around impression roller 24. In this connection, it has been found that urethane and Thiokol (polysulfide synthetic elastomers produced by Thiokol Corporation, Trenton, N.J.) rubberlike impression rollers can be made permanently self lubricating by use of molybdenum disulfide and tungsten disulfide. A heating element 48 can, if desired, be employed to preheat the web prior to its contacting the impression roller 24 in order to improve and facilitate the coating of certain web materials. For example, a preheating unit is desirably used in connection with silicone coating of steel and other metal webs and foils.

After receiving the coating deposit from application roller 26, web 30 travels around guide roller 49 and is directed upwardly toward the intermediate shell section 22 where the transducer elements 50 and 51 are located. Transducer elements 50 and 51 are preferably of sufficient size so as to cover the entire width of the coated web. Each of the transducers is connected to a generator (not illustrated) from which they receive high-frequency electrical energy and convert it to ultrasonic waves, generally in the range of from 20,000 to 25,000 c.p.s. These high-frequency waves produce pressure variations in the solvent which cause minute bubbles to form and instantly collapse. As a result, solvent release or evaporation is thereby greatly facilitated. It should be noted that with some coating formulations, it is believed that the ultrasonic wave treatment also assists in the in situ cross linking or polymerization of the coating formulation.

Another important advantage of the ultrasonic treatment, such as provided by transducers 50 and 51, is that it enables more uniform coating thickness. In this regard, a common problem in reverse roller coating has been that there is a tendency for the coating materials to thin out at the middle of the roller and build up along the outer edges. With ultrasonic treatment of coated webs as disclosed in this application the unevenly applied coatings are smoothed out. In fact, coatings applied by a three-roll reverse coating unit equipped for ultrasonic wave treatment of the coated web favorably compare in quality and uniformity to those applied by offset gravure techniques.

In the illustrated embodiment, two transducer elements are shown. It should be noted, however, that in many coating operations a single transducer element may be used. Generally, positioning the transducer element on the coated side of the web is the most desirable arrangement (such as transducer 51).

Solvent evaporation can be further aided by introducing warm air adjacent the transducer element such as through opening 52 in the unit 20 between bottom portion 21 and intermediate section 22. Heated air from a furnace or other source can be used in this capacity.

It is intended that the principal heating of the web be done by heating units such as 33 or 34. These heating elements should be of sufficient size and output so as to heat the solvent carried on the web substrate to its boiling point.

After being directed past transducer elements 50 and 51, the traveling web is directed around rollers 53, 54 and 55 and 56 to a windup roller (not illustrated). With the present invention windup is not necessary since the traveling web leaves coating unit 20 in a substantially dry condition and can then be directed to a printing unit, or if desired, another coating unit so that multiple layered deposits can be applied to a web material in a continuous operation. In this connection, with the application of multiple coatings to a web substrate, it is sometimes desirable to direct the web 30 after it has received the coating deposit from the impression roller 24 to a second coating unit before the first coating deposit formulation has had the solvent evaporated therefrom. In such operations, multiple coatings can be applied to the web substrate, all of which are dried at the final stage of the coating operation. This latter technique is particularly advantageous where there is to be either chemical or physical bondings between the various coating layers.

Since most of the conventionally available transducer elements are adversely effected by heat, it is desirable to locate these elements away from the heaters 33 and 34.

Examples of coating and printing formulations which may be used in accordance with the method and apparatus of the present invention are described in my copending application entitled "Printing and Coating Compositions," Ser. No. 124,329, filed Jul. 17, 1961 and in my previously referred to U.S. Pat. No. 3,067,056. Additional formulations of coating and ink formulations are described below in the detailed examples which are a part of this application.

In accordance with the present invention, each of these formulations includes a heavy solvent, particularly those of the chlorinated and fluorinated type, such as, for example, methyl chloroform, methylene chloride, trichloroethylene, perchloroethylene, pentachloroethylene, ethylene dichloride, trichloromethane, chlorodifluoroethane, and other fluorinated and chlorinated solvents exhibiting like properties and characteristics. Similarly, various combinations and azeotropic mixtures of these fluorinated and chlorinated solvents may be advantageously used. A typical example of an azeotropic mixture which can be used as the solvent component of a coating or printing formulation consists of 43 percent perchloroethylene and 57 percent 2-Nitropropane (percentages on a volume basis).

Solvents of the type described above offer a number of important advantages when used with the method and apparatus of the present invention. For example, since the fluorinated and chlorinated solvents are "dry" solvents, they do not wet or

hydrate surfaces to which they are applied, even where the surfaces are highly porous or composed of absorptive materials. Another important advantage is that the solvents have unusually high dissolving and suspending capacities particularly when used with ink or coating formulations which include resinous material, fillers and pigments. In this regard, when using these solvents it is possible to provide ink and coating compositions which contain up to as much as 50 percent to 60 percent solids as compared to conventional ink or coating compositions wherein the solid content does not exceed 25 percent by weight.

Another important advantage of the fluorinated and chlorinated solvents is that they are nonpolar and, when combined in printing or coating formulations with various known antistatic chemicals or agents, exhibit anionic or cationic properties. Such printing or coating formulations can be used to change the polarity of a web from a negative charge to a positive charge. Examples of antistatic chemicals or agents which may be used include Arquad S-2C-50 (Armour Chemical Co.), cetyltrimethylammonium bromide, cetylpyridium chloride, and laurylpyridinium chloride. Other antistatic chemicals are described more fully in my copending application Ser. No. 124,329 referred to above.

The fluorinated, chlorinated and like solvents will also readily vaporize at temperatures in the low to intermediate range. For example, many fluorinated solvents will boil at temperatures lower than 32° F. while most chlorinated solvents boil at temperatures between 75° F. and 180° F. In this connection, it has also been noted that when used with the apparatus and method of the present invention practically all of the solvent can be recovered. This feature is particularly important since these solvents are relatively expensive and excessive loss thereof would prohibit their use in commercial printing and coating operations. Low-temperature boiling offers the additional advantages of permitting deposit of the coating operations. Low-temperature boiling offers the additional advantage of permitting deposit of the coating or ink composition to a web or object surface at temperatures which result in very low formulation penetration of the web, thereby enabling unusually thin coatings to be uniformly applied. Coating at these low temperatures as embodied in the present invention is believed to be novel. It is particularly important in a number of coating and printing operations, such as, for example, the iron oxide coating of webs as described in connection with the apparatus shown in FIG. 7, wherein depositing of the resin-iron oxide coating dispersed in a chlorinated or fluorinated solvent, controlled particle alignment and solvent removal are accomplished at unusually high speeds in a single coating unit.

The use of fluorinated and chlorinated solvents with the method and apparatus of the present invention offers another important advantage in that these solvents provide a noncombustible, inert atmosphere. This property of the halogenated solvents is particularly advantageous since it permits the use of techniques such as corona discharge treatment of coated webs without requiring that the entire system be maintained under vacuum conditions. By the present invention, the advantageous polymerization-inducing properties of corona discharge treatment are able to be used on coated webs in a nonvacuum environment to provide in situ polymerization of the deposited coating or ink, as well as other property changing treatment thereof. For example, as is described in the present application, hydrophilic coatings can be changed to oleophilic coatings by means of actinic light treatment without web damage or danger of explosions or fire.

In FIG. 2, another variation of the embodiment illustrated in FIG. 1 employing high-frequency sound waves to effect and facilitate solvent release is shown. In this variation, the coating is uniquely applied by means of an aerosol spray nozzle 60. Nozzle 60 is preferably positioned in section 21 of coating unit 20 with the transducer units 50 and 51 positioned adjacent thereto.

The particular coating formulations which can be advantageously used with the aerosol spraying technique of the present invention are more fully described in the examples below, however, it should be noted that various chlorinated and fluorinated hydrocarbons as well as nitrous oxide and carbon dioxide can be used as the propellant. Suitable additive to the fluorinated and chlorinated solvents for use in aerosol spraying include the glycols, glycol ethers, polyglycols, propylene carbonate, dimethyl sulfoxide, formamide (acting both as a cosolvent and coalescing agent) as well as alcohols, ketones, esters, hydrocarbon solvents and plasticizers of the solvating type.

It is important to note that the aerosol spraying technique of the present invention is not limited to the spraying of liquids but also includes pressurized foam coating (i.e. those coating formulations which include surfactants which produce minute bubbles and give the material a frothy mass). Foam-coating material is particularly desirable for use in coating metals, plastics and textiles.

While not specifically illustrated in FIG. 2, it should be realized that intermediate shell section 22 and hood 23 are positioned over shell section 21 as is shown in FIG. 1 to provide a coating unit 20 identical to that shown in FIG. 1 with the exception of the aerosol coating nozzle 60.

In FIG. 3, a third modification of the ultrasonic solvent release coating unit is illustrated. As is shown, this modification employs a rotogravure printing or coating operation such as that which is more completely disclosed in my earlier U.S. Pat. No. 3,067,057 referred to above. In this modification, web 30 passes around the impression roller 62 and receives a printing or coating deposit from printing cylinder 63. Cylinder 63 may have an overall printing surface or it may carry a design wherein there are printing areas and nonprinting areas. The lower portion of cylinder 63 runs in a liquid bath contained in the bottom of the shell section 21. This liquid bath includes an ink or coating composition which is dispersed or dissolved in a fluorinated or chlorinated solvent. Particular formulations which can be advantageously employed are more completely described below and, are also found in the above-referred to U.S. Pat. No. 3,067,056 and copending application Ser. No. 124,329. When heating is desired, the temperature of the bath may be controlled in any of a number of ways such as by passing a heating fluid (gas or liquid) through a coil 64 located in the bottom of the shell 21. Any fluid heating medium of suitable heat transfer and other physical characteristics may be used, such as steam, oil or Dowtherm (eutectic mixture of phenyl ether and 26.5 percent of diphenyl oxide having a boiling point of 258° C.). While not shown, a coil 32 such as shown in FIG. 1 and 2 may also be provided.

While not specifically shown in FIG. 3, quartz or other semiconductor-type transducers 50 and 51 similar to those shown in FIGS. 1 and 2 are provided near the rotogravure cylinders so that the solvent molecule exciting effect produced thereby is initiated before the solvent molecules are absorbed into the web material. Transducer placement is particularly critical when porous substrates are being printed or coated. The coating deposit or ink containing bath 65 can be continuously fed through a conduit 66 which in turn is supplied by trough 37, conduit 41 and a makeup coating or ink supply, to provide a completely automatic coating or printing operation.

In FIG. 4, a coating apparatus 70 constructed in accordance with another aspect of the present invention is illustrated. Except as hereinafter described, coating apparatus 70 is substantially the same as the three-roll reverse coating apparatus 20 of FIG. 1. Accordingly, the use of like reference numerals in FIG. 4 will denote that components so designated are identical to those described above. It is important to note that the novel solvent recovery hood 23 described more fully in connection with FIG. 1, can also be advantageously utilized in the present embodiment.

In accordance with the present invention, coating unit 70 is equipped for corona discharge treatment of the coated web. As is schematically shown, the corona treatment components

include a generator 71, connected to an electrode 72 and a dielectric covered treater roll 73. Web 30 passes around treater roll 73, receiving the deposit of coating material dispersed in the fluorinated or chlorinated solvent from the nozzle 60 and is then immediately subjected to a high voltage electrical discharge from electrode 72. Treater roll 73 is generally spaced a minimum distance of at least one-sixteenth inch from electrode 72. The particular spacing between treater roll 73 and electrode 72 will, of course, vary in accordance with the output of generator 71 and is best defined as being that which best accomplishes the desired treatment of the coated or printed web. Treater roll 73 is connected to a suitable ground 74.

Electrode 72 produces a spark discharge which jumps the air gap resulting in the corona discharge. Generally, the electrode should be sized so that it produces a corona discharge across the entire width of the web being coated. Commercially available electrodes of the type which include the multiple glass-covered variety, multiple vinyl or acrylic covered type, bare knife edge, or shoe-type electrodes can be advantageously employed.

Generator 71 can usually consist of a tesla coil which is energized by a spark-gap oscillatory circuit. In this connection, it has been found that a voltage of from 19 to 36 kilovolts can be advantageously used to provide a corona discharge which, depending upon the particular coating material being used, will produce the desired results.

It has been found that corona discharge treatment can be advantageously employed to obtain in situ polymerization of the coating deposit, improved bonding of the coating to the web by reason of a permanent charge being placed on the deposited coating material, and better solvent release therefrom.

Polymerization or cross linking of the deposited material generally occurs where the coating or ink deposit is comprised of a dielectric polymer such as paraffin wax, asphaltic sulfurized fossil resins, caruba wax, beeswax, nylon, acrylics, and saran. These ink or coating deposit materials are, in accordance with the present invention, dispersed or dissolved in a fluorinated or chlorinated solvent and, when used in an aerosol application technique such as shown in FIG. 4, suitably combined with a satisfactory pressurizing medium. The temperature at which the coating or ink materials are deposited will vary in accordance with the intended coating operation. As was explained previously, the present invention finds advantageous utility in that it can be used for both low temperature coating (below 32° F.) or, if desired, high temperature coating (up to 180° F.) with substantially complete solvent recovery in both cases.

It is important to realize that the solvent carrying the polymerizable coating or ink deposit is not itself polymerized when subjected to the corona discharge treatment from electrode 72. When the polymerization or cross linking of the coating or ink deposit takes place, there is not believed to be any chemical reaction involving the solvent. However, it has been found that the release characteristics of the fluorinated or chlorinated solvent are thereby greatly increased. While the applicant does not wish to be bound to a particular theory explaining this phenomenon, it is believed to result by reason of the newly formed polymers having a reduced affinity for the solvent.

Coating and ink deposit compositions having a polycrystalline structure provide another advantageous characteristic when subjected to corona discharge treatment as embodied in the present invention. It has been found that improved bonding results by reason of a permanent charge being placed on the newly formed polymers, which charge acts to bond the polymers to the web substrate. In addition to significantly improved bonding, the polycrystalline deposits when subjected to the corona discharge undergo a chemical transformation which provides unexpected and desirable results. For example, a wax-paraffin coating applied to paper when subjected to corona discharge takes on a very high gloss and exhibits physi-

cal properties as it becomes electrified very much like that of an electrically charged surface. This permanent charge improved bonding characteristic is not obtained with the hydrophillic polymers such as regenerated viscose and ethyl cellulose since these materials are not of a polycrystalline structure.

As is illustrated in FIG. 5, corona discharge treatment can be used with rotogravure and other types of printing and coating apparatus. Generator 71 and electrode 72 of FIG. 5 are of the same design and construction as their counterparts in FIG. 4. Dielectrically covered treater roll 73a, however, is shown in spaced-away relation from impression roller 62 in this embodiment, illustrating that corona discharge treatment can be provided at locations other than immediately adjacent to where the coating or printing formulation is applied.

FIG. 6 illustrates another embodiment of the present invention. In this modification ultraviolet polymerization is used for promoting cross-linking of the coating or ink deposit. As was true with corona discharge treatment of polycrystalline coating and printing compositions, improved bonding results with ultraviolet techniques via the placing of a permanent charge on the newly formed polymers.

While aerosol spraying is illustrated as the coating depositing means, it will be appreciated that other coating and printing methods well known in the art may be employed such as rotogravure, reverse roll, etc.

Actinic radiant energy for producing photopolymerization of the coating or ink deposit is provided from ultraviolet lamps 76 mounted on a bar 77 suitably supported at the opening 52 in the coating unit 78. Several makes of ultraviolet lamps are commercially available which can be used for this purpose including those often referred to as sun, Xenon, mercury vapor or quartz lamps. Other sources of radiant energy include cathode ray tubes, lasers, masers and sources of gamma and beta radiation. So-called solar furnaces may also be used where practical.

The solvents which may be employed in this technique are similar to those previously described. They generally have a low boiling point, yield vapors that are heavier than air and are easy to condense. These include methylene dichloride, perchloroethylene, trichloroethylene, Chlorotene NU (Dow), pentachloroethylene, ethylene dichloride, trichloromethane dichloromethane, trichlorotrifluoroethane, trichloromonofluoroethane and hexane, and various mixtures thereof. Aqueous solvents and diphasic systems may also be used.

Among the coating and ink materials which can be advantageously used in connection with the photopolymerization technique described in the present embodiment, are the water soluble hydrophillic polymers such as gelatin, polyampholytes, polyvinyl acetate, polyvinyl alcohol, polyvinylpyrrolidone, isopropyl cellulose (Klusal, Hercules Powder Co.), methyl cellulose, collagen and other proteinaceous matter. These materials are soluble in the fluorinated and chlorinated solvent and can be applied in very thin films to the substrate surfaces. When subject to ultraviolet light they become oleophillic coatings.

FIG. 7 illustrates an embodiment of the present invention having particular utility for high speed coating of a web with an iron oxide-resin composition. With the apparatus shown, it is possible to apply magnetic iron oxide particles on a substrate surface, align these particles in a predetermined and desired arrangement, and then provide in-line treatment of the thus coated web to polymerize the resin and obtain substantially complete solvent recovery.

An important aspect in the coating of iron oxide particles is that the solvent vehicle remains on the substrate surface until such time as the predetermined and desired particle arrangement has been obtained. Accordingly, it is desirable that low temperature coating techniques be applied. In this connection, coil 32 can generally be supplied with a refrigerant or cooling water so as to maintain the temperature in the lower shell portion 21 substantially below the boiling point of the particular solvent employed.

The coating deposit formulation employed in this coating technique generally includes the iron oxide particles, a polymer resin, and a fluorinated or chlorinated solvent. Typical examples of the magnetic iron oxides are those commercially available as IRN-351, IRN-110, IRN-115 and IRN-220 (C. K. Williams Co.). The preferred polymer resins are those which are soluble in the fluorinated or chlorinated solvent such as, for example, an acrylic ester copolymer identified commercially as Hycar 1432 (B. F. Goodrich). The fluorinated and chlorinated solvents include those mentioned above. In using coating formulations containing iron oxide particles, it is highly desirable to provide at the bottom of fountain 28 a high frequency impulse generator 31 of the type described in connection with FIG. 1.

After the coating deposits containing the magnetic iron oxide particles, polymer resin and solvent vehicle are applied to the substrate surface by the roller 63, the coated web 30 travels to a position where it is spaced adjacent to a magnetic field generating unit, schematically illustrated in FIG. 7 and designated by the reference numeral 80. The solvent and polymer resin are still intact on the web substrate because of the low temperatures maintained in this section of the coating unit thereby permitting movement of the particles in accordance with the magnetic influence imparted thereto by particle alignment component 80. The coated web passes from the region directly adjacent the alignment unit 80, to a location in the coating unit where the solvent release means act to facilitate and evaporate the solvent vehicle. If desired, the various polymerization techniques described in the present application can be used to polymerize the resin component of the coating formulation.

As is shown in FIGS. 1, 4, 6 and 7, heating elements 33 and 34 can be used to evaporate the solvent from the coated web or object surface. Any conventional electric or infrared heaters may be employed, the primary requirement being that it have a sufficient output so as to heat the solvent component to its particular boiling point. Similarly, selective heating techniques, as provided by high frequency heating and drying units (such as marketed by the Radio Frequency Company of Medfield, Mass.) may be advantageously employed for unusually quick and thorough solvent vaporization.

The hot metal dip drying technique of the present invention finds utility not only in drying webs to effect solvent removal, but also in removing any electrical charges from webs composed of saran (polyvinylidene chloride), cellulose acetate and like materials.

As is illustrated in FIG. 8, web 30 after receiving a deposit of a coating formulation from aerosol nozzle 60 is directed around guide rollers 85, 86 and 87 into a molten metal bath 88. The temperature of metal bath 88 is maintained by heating elements (not illustrated) at least as high as the boiling point of the particular solvent component of the coating formulation. Similarly, the depth of bath 88 is sized to permit sufficient contact of the coated web with the molten metal for effecting complete drying thereof. In this regard, the bath size will also be directly proportional to the web speed. Typical examples of metals which can be utilized include bismuth, tin, Wood's alloy and lead as well as other metals having melting points ranging from 80° F. to 2000° F.

After entering molten metal bath 88 web 30 is directed around roller 89 upwardly toward coil 90 which is supplied with cold water or a refrigerant for cooling the hot web. While the illustrated embodiment is of a coating operation, it will be appreciated that this rapid drying technique may be utilized in printing operations also. Similarly, molten metal web and object dipping can be used as a pretreatment technique in molding operations as well as in the forming of laminates.

Reference is now made to the following examples for a more detailed explanation of the present invention.

EXAMPLE I

A nylon polyamide coating can be applied to a web in the following manner. The web is first padded or surface coated

with a formulation prepared in accordance with the following relative quantities:

sodium carbonate — 40 parts by weight
hexamethylenediamine — 22 parts by weight
water — 500 parts by weight

The above ingredients are thoroughly mixed and applied via conventional dip coating methods. Following dip coating, the coated web is then directed to a coating unit 20, such as disclosed in FIG. 1 of this application. Fountain 28 of coating unit 20 contains a coating formulation composed of the following ingredients:

sebacoyl chloride — 15 parts by volume
methylene chloride — 500 parts by volume

The temperature of fountain 28 is maintained at about 70° F. with a web speed ranging from 100 to 2,000 feet per minute. This web speed is governed by the padding rate since the entire operation is continuous. Ultrasonic wave treatment at the frequency of 20,000 cycles per second is then imparted to the web immediately after the second coating application.

These high frequency waves serve to activate the methylene chloride thereby facilitating solvent removal. Heaters 33 and 34 provide sufficient output to heat the solvent vehicle contained within the web substrate to 104° F. (the boiling point of methylene chloride). The solvent vapor is then collected and condensed in the solvent recovery hood.

EXAMPLE II

This example illustrates the application of a gelatin coating to a paper substrate via a three-roll reverse coating technique. The coating formulation is first prepared by thoroughly mixing 3,200 ml. of water with 800 grams of 225 bloom gelatin and allowing the mixture to stand about one hour at which time all the water is absorbed by the gelatin to produce a swollen mass. The gelatinous mass is then warmed to between 60° F. and 65° F. and again thoroughly mixed to insure a homogeneous solution with water being added to bring the volume up 4,000 ml. To the above solution, 2,000 ml. of methylene chloride are added in a mixing apparatus equipped for cold water condensing to prevent solvent loss. In this connection, it has been found that methylene chloride having a boiling point of 104° F. and gelatin melting at the same temperature renders the two materials ideally suited for combined use in this coating operation.

The formulation is then placed in fountain 28 and applied by a three-roll technique as previously described. Transducers 50 and 51, heater elements 33 and 34 and solvent recovery hood 23 all cooperate to effect substantially complete solvent recovery.

Other water soluble polymers which can be used in place of or in conjunction with the bloom gelatin include the polyampholytes, polyvinylacetate, polyvinyl alcohol, polyvinylpyrrolidone, isopropyl cellulose (Klusek — Hercules Powder Co.), methyl cellulose, casein glue and similar proteinaceous materials. In addition, the above materials can also be mixed with light sensitized materials such as ammonium or potassium dichromate, silver halide salts, and the like for forming photographic images on the web substrate or forming oleophillic coatings when a light sensitizer is present.

EXAMPLE III

The present example is an illustration of foam coating of gasket materials which can be used for tin can covers, jar closures, and the like. In this example, a web of gasket material receives two separate coatings applied in separate or continuous steps.

The first adhesive formulation is prepared from the following ingredients:

Diethylcyclohexylamine (amine catalyst) — 50 parts (by weight); and
methylene chloride — 50 parts (by weight).

The amine catalyst and methylene chloride are mixed and applied by aerosol spray to the web substrate in accordance with the techniques described in this application. A temperature of 70° F. at the region of adhesive formulation deposit and a web speed of 500 to 2,000 feet per minute can be employed. Vaporization of the methylene chloride can be facilitated by means of ultrasonic treatment of the coated web prior to the heating thereof.

A urethane adhesive composition for the second coat is then prepared from the following ingredients:

One hundred parts by weight of Vorite 101 castor based polyester prepolymer (Baker Castor Oil Co.);
Ten parts by weight glycerine.

If desired, 120 parts by weight of Asbestine (International Pulp Co.) may be added to each 100 parts of adhesive base to increase the bonding of the foamed polymer to the substrate. Also, very finely ground glass fibers or boron fibers may be employed in this connection. An oleophillic lignin polymer filler (West Virginia Pulp & Paper Co.) can also be employed. The above formulation is then dispersed in a chlorinated-fluorinated solvent such as trichlorotrifluoroethane.

The above urethane adhesive is then sprayed on the substrate containing the amine catalyst. Ultraviolet irradiations of the urethane adhesive before application acts to improve the bonding properties of the coating. Other coating and printing techniques can be used with the method of this example to provide selective depositing of the coating in a predetermined design or pattern such as, in the forming of gasket rings on a metal or plastic web which ultimately is stamped into a closure cap.

EXAMPLE IV

The present example relates to an aerosol spraying technique for coating textiles and similar fabrics with a composition which makes their surface highly resistant to water, grease and other stains. It is important to note that the application of these coatings when done in accordance with the present invention results in substantially complete solvent recovery.

The following components are used in the preparation of the coating composition:

	Points by weight
General Electric 33-4034 (dimethyl polysiloxane polymer).....	10
Vinylpyrrolidone (N-vinyl-2-pyrrolidone).....	10
Gantrez AN (inter polymer of methyl vinyl ether & maleic anhydride).....	10
Triethanolamine.....	8
Methylene chloride.....	60
Tributyl tinlaurate.....	2

The vinylpyrrolidone and Gantrez AN are combined and dispersed in methylene chloride and triethanolamine. The dimethyl polysiloxane polymer and tributyl tinlaurate are then added with high speed mixing at a temperature of about 60° F.

This coating formulation is applied by aerosol spray techniques as described in the present application or, if desired, by a trihectical gravure or flexographic engraved cylinder (hectical depth 25 to 35 microns, 120 line screen). The coated web, traveling at a speed of 1,000 feet per minute is then subjected to ultraviolet radiation and thermal energy from heating elements. The highly volatile amine and the solvent are removed completely. Cross linking of the vinylpyrrolidone and methylvinylether maleic anhydride occurs to produce a highly grease and stain resistant coating on the web.

An important aspect of the method described in this example is that the spraying can be done at relatively low temperatures, around 35° F. and below. When porous substrates are coated at these temperatures, they exhibit a great degree of "hold out" (resistance to solvent and polymer penetration) thereby permitting more efficient coating of the textile fabric and offering greater solvent recovery.

EXAMPLE V

The present example is particularly concerned with a coating or printing process wherein a photoelectric, photoconductive or photosensitive coating is placed on a web by 2 gravure or like printing cylinder. The thus coated web is then subjected to corona discharge treatment and an image projected thereon. This image is developed by applying a dielectric negatively charged powder to the web which fuses to the nonexposed or image blocked portions of the web when subjected to heat.

In preparing a photoelectric coating formulation which can be utilized in printing or coating a paper, metal or plastic web, one of the ingredients thereof, the sulfurized asphalt fossil resin, is first prepared from the following materials:

	Points by weight
Syrian or Gilsonite asphalt fossil resin.....	100
Carbon disulfide.....	600
Sulfur chloride.....	8

The above ingredients are heated in a three-neck glass reactor flask equipped with a mixer, condenser and temperature control means. Nitrogen or carbon dioxide can be used to purge the system. During the heating, hydrogen chloride and carbon disulfide are distilled off and recovered. The asphalt fossil resin remaining in the reactor flask then becomes sulfurized and when dried, is in the form of a powder.

A coating formulation is then prepared as follows:

	Points by weight
Methylene chloride.....	50
Sulfurized asphalt fossil resin.....	25
Arochlor 1242 (a biphenyl resin produced by Monsanto Co., St. Louis, Mo.).....	10
Anthracene.....	10
Rose Bengal (cold tar dyestuff).....	1-5

If desired, selenium, copper cadmium sulfide or photox-801 French processed zinc oxide (New Jersey Zinc Co.) may be substituted for the anthracene.

The methylene chloride, sulfurized asphalt resin, arochlor resin and photo-conductive anthracene are thoroughly mixed together with constant stirring. This formulation is then applied to a paper, plastic or metal web traveling at a speed of from 500 to 2,000 feet per minute. The web is coated or printed in halftone dots applied by a photoengraved gravure or flexographic printing cylinder. The density of the halftone dots will vary with the ultimate use, however, a web having 65 or 85 line screen printed halftone dots is desirable for use in forming a photoelectric coating which can be used to receive an image in accordance with this example.

A second formulation which can be used in place of the above formulation is composed of the following ingredients:

	Points by weight
Cadmium sulfide powder.....	10
Hycar 1432 (an acrylic ester copolymer marketed by B. F. Goodrich).....	38
Trichloroethylene.....	50
Rose Bengal.....	2

The cadmium sulfide, Hycar 1432 and trichloroethylene are thoroughly mixed together. The Rose Bengal is then added with constant stirring to insure a uniform distribution throughout the mixture. This coating formulation can be applied in the same manner as was described above in connection with the first formulation, with the temperature in the fountain containing the formulation being maintained at around 70° F.

After receiving either of the above coating formulations the web is subjected to ultrasonic treatment for facilitating evaporation of the solvent.

The thus coated web can be stored for later use or sent directly to a second coating unit where the image is applied thereto. In this regard, it should be noted that the photoelectric halftone dots having good dielectric properties acquire a positive charge when subjected to corona discharge. For example, a corona discharge of from 300 to 600 volts will set up a positive charge on the halftone dots which will be retained for a period of from 30 to 100 seconds. Since these dots are photosensitive the activating or sensitizing step must be done in total darkness. Once the halftone dots are subjected to actinic radiation their charge is almost completely dissipated within a period of from 0.1 to 0.3 seconds.

After the halftone dots on the web have been charged, the web is exposed to actinic radiation through a negative, positive or halftone lined screen in order to set up a latent image thereon. Those portions of the web not exposed to the actinic radiation retain their positive charge while those portions which were exposed quickly become neutralized. The negatively charged powder having self-lubricating properties is dispersed in a fluorinated or chlorinated solvent and applied in accordance with any of the techniques disclosed in this application. During the solvent recovery phase wherein the solvent is evaporated from the web, the heat fuses the negatively charged particles to the positively charged halftone dots on the web substrate. If desired, the negatively charged powder can be applied in a dry form to the exposed web to develop the latent image thereon.

Typical permanent type self-lubricants which can be used include molybdenum disulfide, glass micron fibers, selenium disulfide, tungsten disulfide, amorphous graphite, molybdenum selenide, "Teflon" micron sized fluorocarbon fibre powder, tungsten selenide, tetraethyllead, anthracene, di-n-butyl tin sulfide, Amoco 600 isobutylene polymer (linear), lead, zinc naphthenates and molybdenum xanthates. These materials may be used separately and in admixture depending upon the particular requirements.

Other photoresponsive coal tar dyestuffs and reagents for increasing spectral light response of photoelectric coating or ink which may be used include iodoform, rhodamine B, saffrol, isoeugenol, isosafrol, eugenol methyl ether, bromophenol blue, methyl green, acridine orange, fluorescein, eosin Y, Sudan Brown, erythrosine c.l. 722, phloxine (c.l. 778), victoria green (c.l. 657), brilliant green crystals (c.l. 662), pinacyanol chloride, crystal violet lactone, rhodamine lactone and malachite green lactone.

EXAMPLE VI

The present example is directed to the coating of magnetic iron oxide particles on a web substrate. It can be advantageously used in the manufacture of high quality magnetic recording tape.

The magnetic iron oxide and polymer resin formulation is prepared from the following ingredients:

IRN-351 (C. K. Williams) — 90 parts by weight
Hycar 1432 (B. F. Goodrich) — 25 parts by weight
Amoco 600 (Linear fibrous isobutylene polymer Amoco Chemicals Corp.) — 5 parts by weight
Chlorinated or fluorinated solvent — 50 parts by weight

The above ingredients are thoroughly mixed and applied via the three-roll reverse coating technique such as is illustrated in FIG. 1. The application roller 26 and impression roller 24 are adjusted to provide a 50 p.s.i. pressure on a mylar film web at the point of coating deposits. The coating is applied at a thickness of 2.5 mils. A web speed of 1,000 feet per minute can be used. The application of the formulation containing the magnetic iron oxide is done at a temperature of 32° F. or below so as to insure that the solvent and polymer resin remain intact on the web surface until particle alignment could be obtained. The particle alignment unit is positioned from ¼ to 4 inches from the traveling web and produces a magnetic field of 1,800 gauss. The solvent is then heated to its boiling point by heating units to effect substantially complete

evaporation thereof in accordance with the techniques described in this application.

Other magnetic iron oxide materials which may be employed include IRN-110, IRN-115, and IRN-220 (C. K. Williams Co.) carbonyl iron powder (General Aniline and Film Co.) and also the magnetic iron oxide provided by Indiana General Corp. of Valparaiso, Ind. In addition to Hycar 1432, other polymer resins which can be employed and which are soluble in the chlorinated and fluorinated solvents are the acrylonitrile copolymers, nitrocellulose, abitol, acrylic resins, and other plastic polymeric and fibrous materials having high molecular weights and melting points which anneal thermally with heat, hot oil, and molten metal.

Magnetic recording tape processed according to the present example exhibits a high residual magnetism thereby offering improved low frequency response and output.

EXAMPLE VII

The present example is directed to the coating of a web substrate with dielectric polymer resins followed by subjecting the coated web to corona discharge treatment to set up cross linking or polymerization of the deposited coating and improved bonding by means of the permanent type electrical charging of the newly formed polymers.

The following ingredients are used in preparing the coating formulation:

Micro crystalline wax — 30 parts by weight
Paraffin wax — 30 parts by weight
Chlorothene NU (Dow) — 40 parts by weight

The above ingredients are thoroughly mixed together and placed in the lower section 21 of a coating unit equipped for corona discharge treatment, such as is illustrated in FIG. 5 of this application. The temperature of the formulation is maintained at 100 F. and the web speed maintained at 1,500 feet per minute.

A coating deposit .001 to 5 mils thick is applied to the web 30 via the gravure cylinder 63. Electrode 72 is to 1 inch away from the dielectric treated roller 73a. Generator 71 should furnish sufficient electrical power so as to set up an electrical potential of between 500 and 1,500 volts between electrode 72 and dielectrically covered treater roll 73a.

The temperature in the intermediate shell section is preferably maintained at 180 F. (the boiling point of Chlorothene NU) by means of heating elements 33 and 34. Complete evaporation of the Chlorothene NU from the coated web is accomplished under these conditions.

The coated web prepared in accordance with this example exhibits a superior wax paraffin-microcrystalline copolymer coating which is characterized by a "spectacular gloss" and possesses excellent moisture-oxygen permeability characteristics.

Other high dielectric polymer resin materials which can be used in coating formulations applied in accordance with this example include asphaltic sulfurized fossil resins, carnuba wax, beeswax, nylon, acrylics, and polyvinylidene chloride.

In this example the resinous-polymer, dispersed in a non-polar solvent, becomes electrified when subjected to a high potential corona discharge and can be characterized as an "electret" in that it has both a homocharge and a heterocharge which will not decay even if neutralized. The resinous-polymer compositions when so charged exhibit superior bonds to all substrates. In this regard, gasket formed in accordance with these techniques provide unusual sealing qualities which greatly enhance their value in vacuum closures and the like.

EXAMPLE VIII

This example is directed to the forming of photographic images on webs by depositing on the web substrate a composition which comprises a plastic resin, light sensitive chemicals, organic dyestuffs, and a catalyst. After this formulation is deposited on the traveling web, it is subjected to ultraviolet

radiation, before solvent removal, through a negative or positive film or other image producing means.

The following ingredients are used in preparing the coating formulation:

	Points by weight
Acrylonitrile (resinous material)-----	20
Cinnamyl chloride (light sensitive chemical)----	3
Aeridine orange (organic dyestuff)-----	2
Copper-phenyl-acetylide (catalyst)-----	5
Chlorinated or fluorinated solvent-----	70

The above ingredients are thoroughly mixed together at 32 F. to 70 F. and placed in a vessel pressurized with a refrigerant gas which is connected to a nozzle for aerosol spraying onto a plastic film or paper web. A spraying pressure of 30 p.s.i. is maintained with a web speed of 100 to 2,000 feet per minute. The preferred temperature range at the point of depositing of this formulation onto the traveling web is between 32 F. and 70 F. After the coating formulation has been deposited on the web substrate, it is then subjected to irradiation by ultraviolet lamps of 1,200 to 4,600 angstrom units, each of which is spaced 1 to 8 inches from the traveling web. Interposed between the traveling web and the ultraviolet light source is an image producing film.

Other resinous materials which can be employed include vinyl pyrrolidone, gelatin, polyvinyl alcohol, dialdehyde starch, and protein polymers. Other coal tar dyestuffs which can be employed include bromophenyl blue, pinacyanol, and erythrosin. Other light sensitive chemicals which can be used include copper-cadmium sulfide, iodoform, anthracene, and 2, 2, 1Azobis-isobuty acrylonitrile. Catalysts which can be advantageously included are benzoyl peroxide 7, 7, 8, 8-tetracyano quinodimethin, and dibutyl tinlaurate.

Techniques other than ultraviolet ray treatment of the coated web which are used to set up the image include X-ray, visible light, infrared and electron beam.

EXAMPLE IX

The present example is directed to a method of preparing microfine pigment particles having uniform oleophillic coatings which remain effective even after the particles undergo grinding or other size reducing operations. These particles can be used as dielectric powders, as described in Example V or, can be dispersed in a fluorinated or chlorinated solvent and applied to a web or object surface.

The following ingredients are used in a typical formulation:

	Points by weight
Molybdenum disulfide-----	10
Micro-size glass fibres (fiberglass)-----	5
"Teflon" micron size glass fibres-----	5
"Hycar" 1432 acrylic ester copolymer (B. F. Goodrich)-----	10
Chlorothene NU (Dow Chemical Co., Midland, Michigan)-----	70

These ingredients are combined in a fountain equipped with a dispersing means such as, for example, a Cowles Mixer. Ultrasonic generator-transducer units of the type identified by the reference numeral 31 in the present application may be advantageously used in conjunction with a Cowles Mixer to insure uniform size reduction and thorough mixing. A refrigerated condensing unit is employed to maintain the temperature in the fountain at 32 F. or below. These materials are thoroughly mixed together until all of the pigment particles have been uniformly coated.

The formulation is applied directly to a paper, metal or plastic web by any of the techniques described in the present application and then subjected to ultrasonic wave treatment and heat for solvent vaporization.

If desired, the reinstated or oleophillic coated pigment particles may be dried by heating the fountain to drive off the solvent. In this regard, a solvent recovery hood of the type described in this application can be advantageously used to collect and condense the solvent vapors. When dried the resinated pigment particles can be shipped or stored for subsequent use.

The oleophillic coatings obtained by this method are significantly improved over those produced by conventional fatty acid treatment since these coatings are polymerized and more permanent.

Generally, where a monomer is used in the formulation, a catalyst is necessary to effect polymerization. Polymeric resins, such as the acrylic ester copolymer used in the above formulation, do not generally require the presence of a catalyst for this purpose.

Other permanent type self-lubricants which may be used either alone or in combination with the molybdenum disulfide include Amoco 600 linear isobutylene polymer (Amoco Chemicals Co.), Microthene (U. S. Industrial Chemicals Co.), polyethyethylene spherical micron beads, micro glass beads, boron micron fibers, tungsten disulfide, molybdenum selenide, tungsten selenide, graphite "Teflon" micron size fluorocarbon powder, anthracene, ferrocene, micron size nylon polycaprolactum heat stabilized powder, tetraethyl lead, di-n-butyltin sulfide and molybdenum xanthate.

EXAMPLE X

This example is concerned with ultra-thin protective coatings for webs and object surfaces composed of paper, metal, plastic and the like.

A typical formulation is composed of the following ingredients:

	Parts by weight
Vinyl chloride monomer.....	20
Trichloroethylene.....	80

These ingredients are thoroughly mixed in a refrigerated mixing container chilled to 32° F. or below. This formulation is then supplied to a refrigerated fountain of the type shown in FIG. 1 and deposited onto a web surface. Any of the coating methods described in this application may be used. The monomer-solvent formulation forms a thin film on the web which, when subjected to corona discharge, polymerizes the monomer component. The potential between the electrode and dielectrically coated treater roll is preferably from 500 to 10,000 volts with the electrode being spaced about one-eighth inch from the coated web.

Other materials which may be substituted for the vinyl chloride monomer include ethylene, acrylic, fluorine and poly-para-xylylene type monomers.

EXAMPLE XI

This example is directed to the coating of textile, paper, plastic and metal webs or objects surfaces with silicone dimethylpolysiloxane polymers which form insoluble inert coatings on the web or object surface.

The following ingredients are used in preparing the coating formulation:

	Parts by weight
Silicone dimethylpolysiloxane polymer.....	20
Chlorothene NU (Dow Chemical Co., Midland, Michigan).....	78
Tributyl tinlaurate (or other suitable catalyst).....	2

The above ingredients are thoroughly mixed together and applied to the web substrate at 32° F. This low temperature enables the coating to be uniformly applied in thicknesses of from monomolecular up to 2 mils thick. The thus deposited web is then subjected to ultraviolet irradiation wherein the silicone polymer in the presence of a catalyst is polymerized. Four ultraviolet light lamps spaced a distance of 1 to 8 inches from the traveling web, each being of 2,200 to 2,800 Angstrom units, are used with a web speed of 100 to 3,000 feet per minute.

After the ultraviolet irradiation, the coated web is subjected to high frequency waves, (25,000 cycles per second) to improve the bonding properties of the silicone polymer and facilitate solvent release. The solvent is heated to 180° F. (boiling point of Chlorothene NU) and the evaporated solvent vapor collected and condensed in the solvent recovery hood.

In this example, it is important to note that the silicone polymers are advantageously applied to web substrates at low temperatures, 32° F. or below since at these temperatures they have a low viscosity index when dispersed in chlorinated or fluorinated solvents. The techniques described in this example can also be used to provide combined epoxy-polyamide resin coatings to webs and object surfaces.

EXAMPLE XII

The present example is directed to the coating of paper, plastic and metal webs with tung or safflower oil coating formulations. The techniques described in this example are particularly useful in coating of tin can bodies and lids.

The coating formulation includes the following ingredients:

	Parts by weight
Nonconjugated tung oil.....	20
Conjugated tung oil.....	10
Chlorinated paraffin.....	10
Aluminum oxide (catalytic grade).....	2
Aluminum chloride solvated in propylene carbonate.....	2
Cinnomyl chlo. ide (light sensitizer).....	2
Iodoform.....	1
Chlorinated or fluorinated solvent.....	44

The above ingredients are thoroughly mixed together at 70° F. In this connection, it should be noted that mercaptides, resinated or coal tar color dyestuff progenitors which are capable of condensing, chelating, degrading or otherwise complexing the Fridel-Crafts catalyst in presence of ultraviolet irradiation may be substituted for the iodoform.

The above formulation is applied by means of any of the techniques described in the present application and then subjected to ultraviolet light resulting in the formulation of complexes which become highly bonded to the substrate. The temperature in the intermediate zone of the coating unit is maintained at the boiling temperature of the chlorinated or fluorinated solvent for effecting substantially complete evaporation of the solvent from the web substrate.

In the coating of a tin can surfaces, it is desirable that the coating formulation be applied in thickness of less than 1 mil by either aerosol or offset gravure techniques.

EXAMPLE XIII

This example relates to a method of treating "nonprintable" surfaces with a polymerizable coating formulation that acts as a good receptive surface for ink and coating deposits. Examples of the "nonprintable" surfaces which can be treated in accordance with this method are those composed of polyvinyl fluoride, polytrifluoroethylene, polytetrafluoroethylene, polyesters, polypropylene and polyethylene.

A typical coating formulation includes the following ingredients.

	Parts by weight
Tung oil fatty acid.....	5
Toluene sulfonic acid.....	5
Trichloroethylene (chlorinated solvent).....	80
Scrap acrylic resin (resin bonding vehicle).....	10

The above ingredients are thoroughly mixed while being maintained at a temperature of from 160° F. to 180° F. The formulation is then applied to the web or object surface to be treated by the aerosol or foam coating method described in this application. Depositing of the aerosol or foam formulation at low temperatures (around 32° F.) is desirable. Ethylene oxide or hexafluoroacetone is included in the aerosol or foam coating formulation.

The coated web is then subjected to corona discharge treatment which polymerizes the coating deposits and activates the polymer surface.

Ultraviolet irradiation can be used in conjunction with the corona discharge treatment. Also, ultrasonic wave treatment of the coated web can be used in combination with these polymerization inducing techniques to improve the coating.

Sulfur trioxide may be used either in place of, or in combination with, the toluene sulfonic acid or tung oil fatty acid. Also, if desired, a pigment or coloring can be added to the formulation to provide a colored coating.

EXAMPLE XIV

This example is particularly concerned with coating or printing of paper, plastics and metals with inks or coatings which contain high atomic numbered pigments which backscatter beta rays to a detection system containing low emitting radioisotopes.

The following ingredients are used in preparing the ink or coating formulation:

	Parts by weight
"Zein" (Corn Products Co.) resinous material.....	20
Methylene chloride (chlorinated or fluorinated solvent).....	70
Bismuth oxychloride—BiOCl (High Z beta emitter, high atomic numbered pigments)---	10

The above ingredients are thoroughly mixed together at 32° to 70° F. The preferred temperature for depositing this formulation as a coating or ink onto the traveling web is between 32° F. and 70° F. After the coating or ink has been deposited on the web substrate, it is then subjected to ultrasonic sound and thermal heat to evaporate the solvent.

Other resinous polymer materials which can be employed include polyvinyl alcohol, polyvinyl acetate, gelatin, thiolated gelatin, silicone esters, fumaric rosin and shellac.

Other high Z beta emitter pigments which can be employed include: bismuth oxychloride, lead tungstate, barium tungstate, litharge, thorium oxide, iodoform, phosphotungstic acid type pigments, and cadmium sulfide pigments.

A radioisotope which can be used in this process are those which emit low energy not exceeding about 0.3 m.e.v. (millelectron volts) and alpha emitters, such as polonium. Examples of such radioisotopes are hydrogen 3, carbon 14, nickel 63 and polonium. The radioisotopes carbon 14, in the form of barium carbonate, calcium 45 in the form of calcium chloride, sulfur 35 in the form of barium or cadmium sulfide, promethium 147 in the form of nickel chloride; all of which emit pure beta rays. These radioisotopes are produced in atomic piles or by means of a cyclotron and may be purchased from the Atomic Energy Commission, Oak Ridge, Tenn.

EXAMPLE XV

This example concerns a method of providing glass bottles and containers with a colorless, ultraviolet absorbent, abrasion-resistant, protective coating. Accordingly, food products which are adversely effected by ultraviolet rays can be safely

packaged in clear containers coated in accordance with this method so as to be in full view to the purchaser and without danger of deterioration caused by sunlight or other sources of actinic radiation. As such, this method eliminates the need for amber and brown colored containers.

A typical colorless coating formulation includes the following ingredients:

	Parts by weight
Acrylic scrap resin.....	6
"Tinopal SFG" (Geigy Dyestuff Co., New York—naphthotriazolystilbene derivative exhibiting advantageous UV absorbing properties).....	2-4
Toluene sulfonic acid or glacial acetic acid.....	2-4
Ethylene dichloride.....	86

In preparing the coating formulation the ethylene dichloride, acid component and acrylic scrap resin are first thoroughly mixed. The ultraviolet absorbent dyestuff is then added. "Tinopal PCR" (Geigy Dyestuff Co., New York) may be substituted for, or used in conjunction with the "Tinopal SFG."

The glass containers are preferably coated while still hot immediately after they exit the molding machine. The coating can be done either by dipping of the bottles in a bath containing the above formulation or by the aerosol spraying techniques described in this application.

The provision of an ultrasonic generator and transducer unit in the formulation bath insures uniformity of the coating formulation applied to the object surface.

The necessity for supplying external heat to vaporize the solvent component will be determined by the boiling point of the particular solvent employed and the temperature of the bottles being coated.

The acrylic resin in the above formulation can be replaced by various silicone and other polymer resins.

In the above formulation, the acrylic resin furnishes the advantageous abrasion resistant qualities of the coated bottles. The toluene sulfonic acid or glacial acetic acid functions to bind the coating to the object surface.

EXAMPLE XVI

The present example is directed to the manufacture of novel electroluminescent panels. The coating techniques of the present invention employing the use of fluorinated and chlorinated solvents are particularly useful in making these panels since these solvents are dielectric and nonpolar and, as such, do not interfere with or disturb the electroluminescent conductive properties of the coatings.

The panel consists of two members which are adhered together or joined by any appropriate means.

The first member is composed of an aluminum foil on which an electroluminescent coating is applied. This coating is prepared from the following ingredients:

	Parts by weight
Acrylonitrile polymer.....	15
Cadmium sulfide or copper cadmium sulfide.....	15
Chlorinated or fluorinated solvent.....	70

The second member is composed of a plastic film on which is applied a pair of coatings. The first of these coatings is in the nature of a partially conductive primer layer while the second coating is characterized by more efficient electrically conductive properties.

In selecting the web material to be used to form the second member, it should be noted that since the light radiation in the finished panel is to be transmitted therethrough, the web should be of a transparent or translucent material. Typical examples of films which may be used include cellulose acetate, "Mylan" (E I. Du Pont) a polyester plastic film, polyvinyl fluoride, polypropylene, polytetrafluoroethylene and polytrifluorochloroethylene.

In forming the second member, the following ingredients are used in a typical coating formulation for the primer layer:

	Parts by weight	
Stannous Tin chloride.....	10	5
Toluene sulfonic acid.....	10	
An azeotropic mixture composed of 43% per-chloroethylene and 57% 2-nitropropane.....	80	

These ingredients are combined and thoroughly mixed together at a preferred temperature of 70° F. The formulation is deposited as a coating on the web at a preferred temperature of between 104° F. and 114° F. Offset gravure or aerosol spray techniques are preferred for this step. The solvent component of the thus coated web is heated to 160° F. (the boiling point of the azeotropic mixture). In this regard, if desired, ultrasonic wave treatment can be used to promote cavitation of the solvent and thereby facilitate the removal thereof. As before, the solvent vapor is collected and condensed in a solvent recovery hood.

After being coated and dried, the plastic web is then coated with a second formulation prepared from the following ingredients:

	Parts by weight	
7,7,8,8-tetraacyanoquinodimethan.....	20	25
Hycar 202 (acrylic ester copolymer B. F. Goodrich).....	10	
Methylene chloride.....	70	

These ingredients are combined and thoroughly mixed together at a preferred temperature of 104° F. and deposited on the web at a preferred temperature range of between 32° F. and 104° F. The ultrasonic wave treatment can, if desired, be used to facilitate solvent removal. The solvent component is heated to 104° F. and the solvent vapor is collected and condensed by means of the solvent recovery hood.

Other resinous copolymers which may be substituted in place of "Hycar 202" are N-vinyl-2-pyrrolidone; tung oil varnish, epoxy resins, polyamide resins, and nylon polyamide resins.

After each of the above coated members are formulated, they are joined together in a sandwich construction by placing the luminescent coating of the first member in intimate contact with the electrically conductive coating of the second member. Connecting the foil backing or substrate of the first member and the primer layer of the second member to a suitable power supply will result in the activation of the luminescent coating. Suitable means for keeping the respective panel members secured together in the sandwich construction include ultrasonic or heat sealing techniques.

EXAMPLE XVII

This example concerns a novel colorless "carbon" paper. In accordance with this example, the colorless transfer coating composition when in contact with a substrate surface which includes a tannin (wood tannin or tannic acid), inorganic clay material, and metal salt ion exchange materials such as, for example, sodium dichromate, will produce a black transfer image on the substrate surface. The colorless composition which can be applied as a backing to a paper web is composed of the following ingredients:

	Parts by Weight	
Crude crystal violet carbinol.....	80	
Unoxidized hematoxylin (logwood).....	50	
Methylene chloride.....	1,000	
Benzyl trimethyl ammonium hydroxide (36% aqueous solution).....	10	

The above ingredients are combined and the mixture stirred with heat for one hour at the reflux temperature. The residue is a light tan solution which, after filtering at about 75° C. and cooling, results in a white crystalline product which has a melting point of 100° C. This colorless product has the charac-

teristic of producing a jet black stain with a strong violet tone when contact with a tannic acid-metallic salt.

The specific coating formulation to be applied to the paper web includes the following ingredients:

	Parts by Weight	
The crystal product produced by the present method.....	20	
Methylene chloride.....	50	
Starch.....	20	
Bentonite clay.....	10	

The above ingredients are combined and thoroughly mixed together and applied to the paper web by aerosol spraying or gravure methods. If desired, ultrasonic wave treatment can be used to cavitate the solvent component. After being subjected to the ultrasonic treatment, the methylene chloride is evaporated from the web by heating to 104° F. (the boiling point of this particular solvent).

Other crude coal tar colorless carbinols include 3, 3 bis (P-dimethylaminophenyl) 6-dimethylamino phthalide crystal violet lactone; 3, 3, bis (P-dimethylaminophenyl) phthalide malachite green lactone; 3, 7, bis (diethylamino) -9-(O-Carboxy) Xanthene rhodamine -B-N-phenylactam; and 3, 3, bis ((P-dimethylaminophenyl) 4, 5, 6, 7 tetrathloro phthalide blue lactone.

Other materials which can be substituted for the logwood include Brazil Wood (Hypernic), Persian Berries, Cochineal, fustic, gall, Quebracho and catechols. Similarly, if desired, protein or cellulosic polymers may be substituted in place of, or used in conjunction with the starch.

The substrate used in conjunction with the above coated paper is prepared from the following ingredient:

	Parts by Weight	
Natural wood tannin.....	10	35
Ferrous iron sulfate.....	10	
Bentonite clay or inorganic mineral clays.....	20	
Methylene chloride.....	60	
Raylig TA (sodium lignosulfonate, Rayonier, Inc.).....	20	40

The above materials are thoroughly combined and applied to a paper web by means of any of the coating techniques described in this application. Polymerization of the coating by the ultraviolet radiation techniques to this application may be employed. Similarly, ultrasonic wave treatment may be used to facilitate solvent removal.

Tannin acid or pyro-gallic acid may be substituted in place of or used in conjunction with the natural wood tannin in the above formulation.

EXAMPLE XVIII

This example relates to aerosol foam coating of substrates. In particular, it concerns the use of collapsible foams which, when subjected to ultrasonic wave treatment collapse and coalesce into uniform film coatings.

Bentonite colloidal clay, color pigments, dyestuffs and inorganic fillers such as titanium dioxide and zinc oxide may be incorporated into the aerosol foam to produce the desired color and opacity in the coating.

Polymers, resins, starches and proteins may be incorporated into the aerosol foam coating for improved bonding and film forming characteristics.

The following ingredients are used in a typical coating formulation:

	Parts by Weight	
Polawax A 31 (Croda Co., New York, a mon-ionic emulsifying wax).....	3.5	65
Methylene chloride.....	51.9	70
Propylene glycol.....	6.0	
"Gentron 11" (Allied Chemical Co. trichloro-monofluoromethane).....	4.0	
Distilled water.....	33.6	
Polyvinyl pyrrolidone.....	10.0	75
Pigment or color component.....	10.0	

It should be noted that there are a variety of polymeric resinous materials which may be substituted in place of or used in conjunction with the polymeric constituent identified above. These include, for example, hydrolyzable proteins, cellulosic polymers, starches and the like.

The above ingredients are combined, mixed and pressurized for aerosol spraying. Any of the propellants described in this application may be used in place of the "Gentron 11" or in conjunction therewith. In this regard, it should be noted that these propellants also act as cosolvents.

After being applied to the web or object surface, the foamed coating is subjected to ultrasonic treatment causing the foam to collapse (degas) and coalesce to provide a uniform coating.

The coated web is then heated in order to vaporize the solvent constituent of the coating formulation. The vaporized solvent is collected and condensed in the novel solvent recovery hood of this invention.

EXAMPLE XIX

The present example concerns a method of coating webs or object surfaces composed of paper, metal, plastic woven cellulosic fibers, etc. In particular, this example relates to coating formulations which have incorporated therewith a monomer or monomeric material. These monomers and monomeric materials when applied to a web or object surface in accordance with the method of the present invention are polymerized to form protective coating exhibiting good oxygen barrier properties.

A typical coating formulation includes the following:

	Parts by Weight
Vinyl monomer-----	10
Methylene chloride-----	85
Benzoyl peroxide (catalyst)-----	5

The above ingredients are combined and thoroughly mixed together with the temperature of the mixture maintained at 32° F. or below. This low temperature is critical since the monomers and monomeric material are highly reactive at room temperature.

This formulation can be applied by gravure cylinder or aerosol spray to the web substrate and then subjected to a magnetic field and corona discharge simultaneously. The combined effect of both these web treating techniques results in a significantly improved polymerized coating. While the applicant does not wish to be confined to a particular theory for the explanation of this unusual improved coating, it is believed to be due to the coupling, cross-linking and cleavage of the polymer chains.

After being subjected to this simultaneous treatment, the coated web is then heated, with the solvent component thereof being vaporized and collected in the solvent recovery hood.

Other monomeric materials which may be used in this coating formulation include isocyanates, saturated and unsaturated polyesters, vinyl monomers, styrene monomers, isobutylene monomers, ethylene monomers, silicone monomeric materials, fluorine monomeric materials and acrylic monomers.

EXAMPLE XX

This example is directed to the forming of resinated pigments in order to impart oleophilic properties thereto. In this connection, it should be noted that organic and inorganic color pigments and dyestuffs when in a press cake form exhibit hydrophilic properties due to the surface of these particles having an aqueous coating. As such, the particles tend to agglomerate and exhibit hydrophilic properties which are generally undesirable for use in coating of web or object surfaces.

A typical formulation includes the following ingredients:

	Parts by Weight
Lithol red water press cake-----	20
Linseed oil-----	60
Methylene chloride-----	20

The lithol red press cake is in an agglomerate form and usually contains from 20 percent to 30 percent water. This water concentration is characterized by aqueous coatings on each of the pigment particles. Other organic and inorganic pigments and coal tar dyestuffs which may be substituted or used in conjunction with the lithol red include hansa yellow, iron blue, phthalocyanine blue and green, chrome yellow, phosphotungstomolybdate toners, complex salts of cationic basic coal tar dyes, inorganic clays, zinc oxide, titanium dioxide and the like.

Other materials which can be substituted for the linseed oil include soya, safflower, and tung oil, and various monomers, monomeric substances, polymers and resinous matter which can be solvated in chlorinated and fluorinated solvents including, for example, unsaturated monomers such as vinyl acetate, styrene, vinylidene chloride, acrylates, acrylonitrile and the like.

The linseed oil and the methylene chloride in the above formulation are first thoroughly mixed together and cooled to 32° F. or below in a mixing apparatus equipped with a Cowles mixer blade. The lithol red press cake is then added. Since the temperature of the solvent and oil is below the freezing point of water, the aqueous coatings on the pigment particles quickly freeze and separate from the pigment particles, enabling the linseed oil to be coated on the respective pigment particles. The Cowles mixer breaks up the agglomerates and insures uniform coating of the respective pigment particles.

If desired, CO₂ or N₂ may be bubbled through the bath in order to maintain the same at the predetermined low temperature (32° F. or below). Also, uniform dispersion and disintegration of the pigment particles can be provided for by the use of an ultrasonic transducer and generator unit, such as that described in the present application and identified by the reference numerals 31.

After the pigment particles have been coated with the linseed oil, heat is applied in order to vaporize the solvent and water. A solvent recovery hood of the type described in this application can be advantageously used to collect and condense the solvent (methylene chloride). If desired, ultrasonic treatment at this step of the operation can be used to promote solvent cavitation and facilitate vaporization. The residue remaining is a resinated pigment particle product exhibiting advantageous oleophilic properties.

EXAMPLE XXI

This example is directed to a collagen coating technique which embodies the use of the heavy solvents and coating methods referred to in the present application.

The coating formulation is prepared from the following ingredients:

	Parts by Weight
Collagen-----	40
Citric acid-----	10
Water-----	40
Methylene chloride-----	100

The citric acid, water and methylene chloride are thoroughly combined and maintained at the melting point of the collagen (around 105° F.). To this mixture, the collagen is added with stirring until a gelatinous mass is formed. The methylene chloride is then added with stirring to provide a heterogeneous mixture which is then uniformly applied to a web substrate in accordance with the techniques described in the present application.

Under certain circumstances, it is desirable to pretreat the collagen mass-solvent mixture with ultrasonic dispersion

means in order to depolymerize or fluidize the mass. In this regard, it should also be noted that a Cowles mixer can be advantageously used to insure uniformity of the coating formulation.

Other acids which may be substituted or used in conjunction with the citric acid include lactic, tartaric and various solid-type acid materials.

While this example has been particularly concerned with the applying of the collagen formulation as a coating on a web substrate by gravure, aerosol and like techniques, it should be noted that this formulation can be extruded, molded, cast or preformed, etc. to provide a filmlike product.

While in the foregoing specification, detailed explanations of the various embodiments of the present invention have been set forth for the purpose of explanation, many variations may be made by those skilled in the art without departing from the spirit and scope of this invention as set forth in the appended claims.

I claim:

1. Apparatus for coating an article, said apparatus comprising a casing having an article-receiving inlet and an article-discharging outlet, means for transmitting an article to be coated from said inlet through a plurality of treatment stages in said casing to said outlet, a first treatment stage in said apparatus located along the path of said article-transmitting means and downstream of said inlet, said first treatment stage including application means operatively connected to a supply of a coating formulation which includes a coating component dispersed in a solvent vehicle, said application means being positioned in said casing and along the path of said transmitting means for depositing said formulation onto said article, a second treatment stage in said apparatus located along the path of said article-transmitting means and downstream of said first treatment stage, said second treatment stage including a transducer means operatively associated with an ultrasonic generator means, said transducer means being positioned in said apparatus to direct ultrasonic waves on said article after said coating formulation has been deposited thereon by said application means, a third treatment stage in said apparatus located along the path of said article-transmitting means and downstream of said first treatment stage, said third treatment stage including a heater means positioned to direct thermal energy onto said article after said transducer has directed ultrasonic waves thereon, whereby said second and third treatment stages cooperate to provide improved solvent release from said article after said formulation has been deposited thereon.

2. The apparatus of claim 1 wherein said casing includes a solvent recovery hood located adjacent said second and third treatment stages, said solvent recovery hood including an inlet through which evaporated solvent is received in a solvent vapor condensing chamber, said chamber being defined by inner and outer walls through which a coolant is circulated, a condensed solvent outlet in said hood communicating said solvent vapor condensing chamber with said supply of coating formulation, and vacuum means communicating with said solvent vapor condensing chamber, whereby said hood is adapted to operate at a pressure below that at which said coat-

ing formulation is applied to said article for facilitating solvent recovery in said apparatus.

3. The apparatus of claim 1 wherein said application means comprises a nozzle and said coating formulation supply includes a pressurized gas source for pressurized spraying of said coating formulation onto said article.

4. Apparatus for coating an article with a formulation which includes a polymerizable component and a solvent vehicle, said apparatus comprising a casing having an article-receiving inlet and an article-discharging outlet means for transmitting an article to be coated from said inlet through a plurality of treatment stages in said casing to said outlet, a first treatment stage in said apparatus located along the path of said article-transmitting means and downstream of said inlet, said first treatment stage including application means operatively connected to a supply of a coating formulation which includes a polymerizable component dispersed in a solvent vehicle, said application means being positioned in said casing and along the path of said article-transmitting means for depositing said formulation onto said article, a second treatment stage in said apparatus located along the path of said article-transmitting means and downstream of said first treatment stage, said second treatment stage including an electrode and dielectrically covered member adapted to provide a corona discharge therebetween, said electrode and dielectrically covered member being positioned in said apparatus with respect to said article-transmitting means to subject said article with corona discharge after said coating formulation has been deposited on said article to promote polymerization of said polymerizable component in said formulation in situ on said article, and a third treatment stage in said apparatus located along the path of said article-transmitting means and downstream of said second treatment stage, said third treatment stage including a heater means positioned to direct thermal energy onto said article after said article has been subjected to corona discharge in said second treatment stage for promoting release of solvent from the coating formulation which was deposited on said article.

5. The apparatus of claim 4 wherein auxiliary solvent release means is provided for facilitating release of the solvent component in said formulation after said formulation has been deposited on said article, said auxiliary solvent release means being positioned in said casing along the path of said article-transmitting means between said second and third treatment stages, said auxiliary solvent release means including a transducer means operatively associated with an ultrasonic generator means, said transducer means being positioned to direct ultrasonic waves on said article after said article has been subjected to corona discharge, whereby said auxiliary solvent release means and said heater means cooperate to provide improved solvent release from said article after said formulation has been deposited thereon and after polymerization and crosslinking of said polymerizable component has taken place.

6. The apparatus of claim 4 wherein said application means comprises a nozzle and said coating formulation supply includes a pressurized gas source for pressurized spraying of said coating formulation onto said article.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,565,039 Dated February 23, 1971

Inventor(s) Robert K. Remer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 10, "treating" should read --treatment--

Column 3, line 59, "for" should read --from--

Column 6, lines 38 and 39, delete "operations. Low-temperature boiling offers the additional advantage of permitting deposit of the coating"

Column 11, line 58, "proteinationous" should read --protein--

Column 12, line 44, "Points" should read --Parts--

Column 13, line 5, "2" should read --a--

Column 13, line 17, "Points" should read --Parts--

Column 13, line 32, "Points" should read --Parts--

Column 13, line 57, "Points" should read --Parts--

Column 14, line 39, "an" should read --and--

Column 15, line 39, after "is" insert --1/8--

Column 16, line 6, "Points" should read --Parts--

Column 16, line 29, "pyrrololidone" should read --pyrrol--

Column 16, line 52, "Points" should read --Parts--

Column 17, line 1, "reinstated" should read --resinated--

Column 20, line 73, "Mylan" should read --Mylar--

Column 22, line 23, "bixtogibyl" should read --boxoxyphenyl

Signed and sealed this 26th day of September 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents