PRINTING AND COATING METHOD

Original Filed May 14, 1965 3 Sheets-Sheet 1

Fig. 1

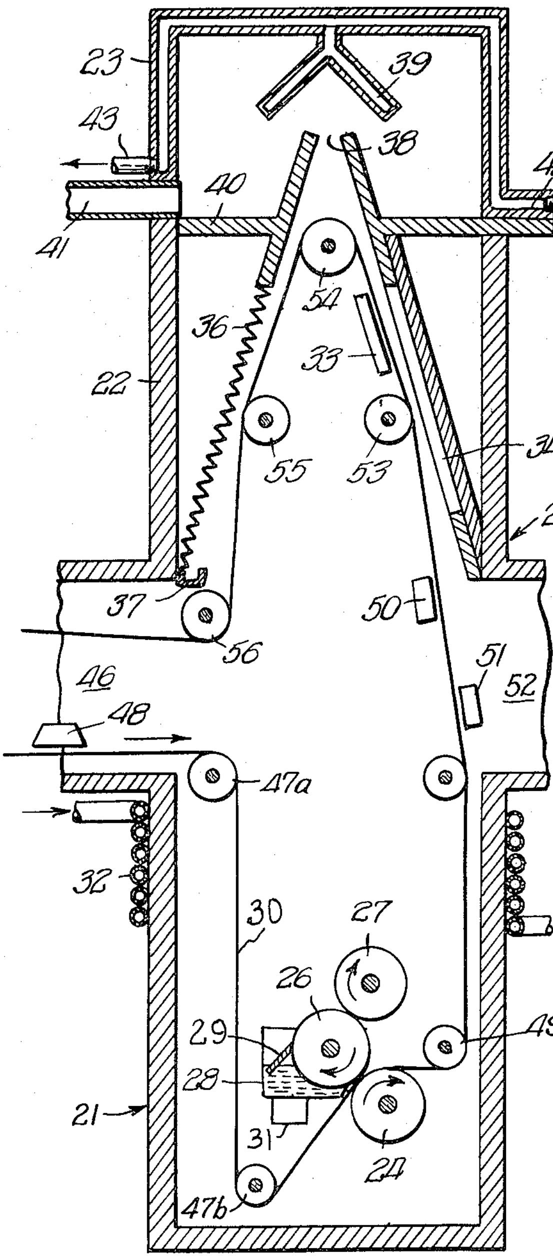


Fig. 2

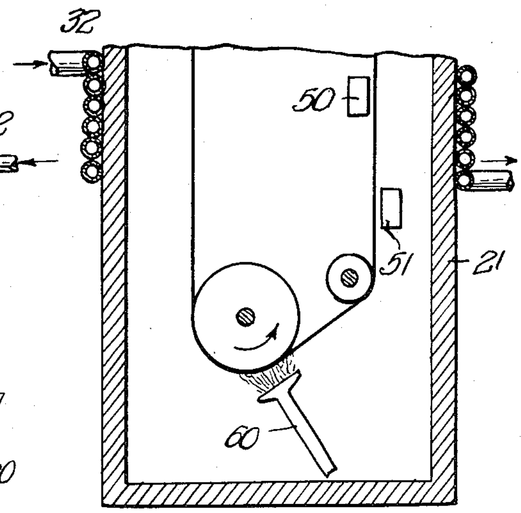
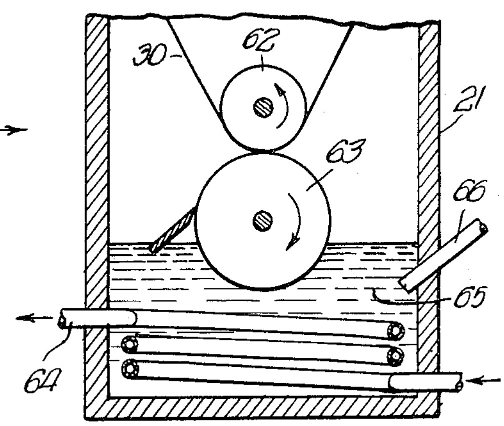


Fig. 3



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PRINTING AND COATING METHOD

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Fig. 4

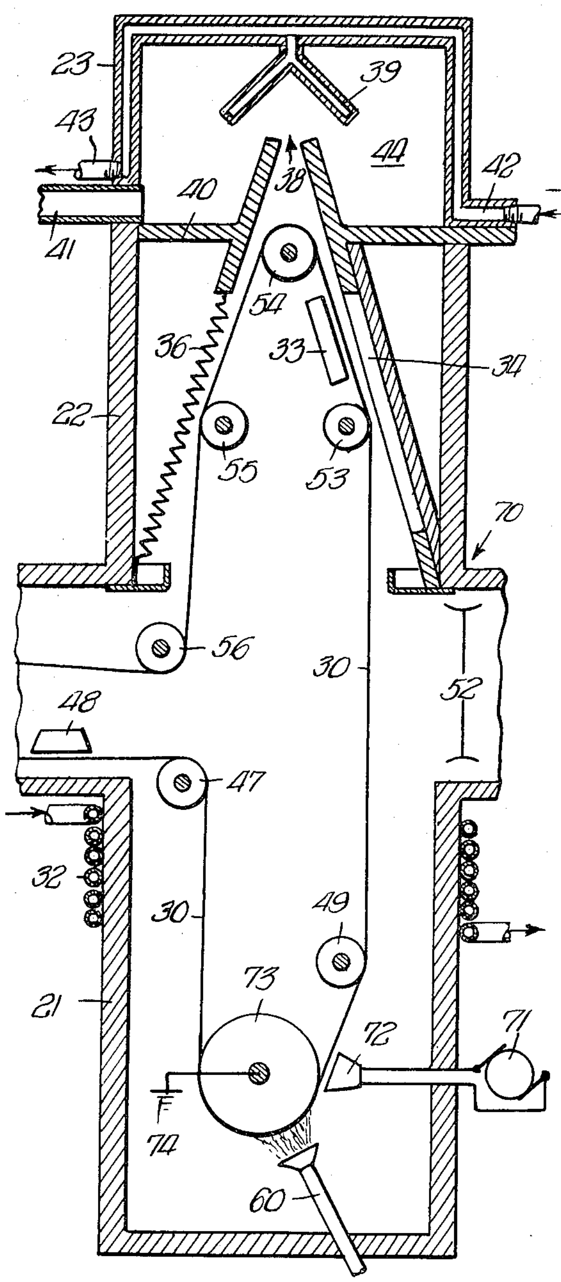


Fig. 5

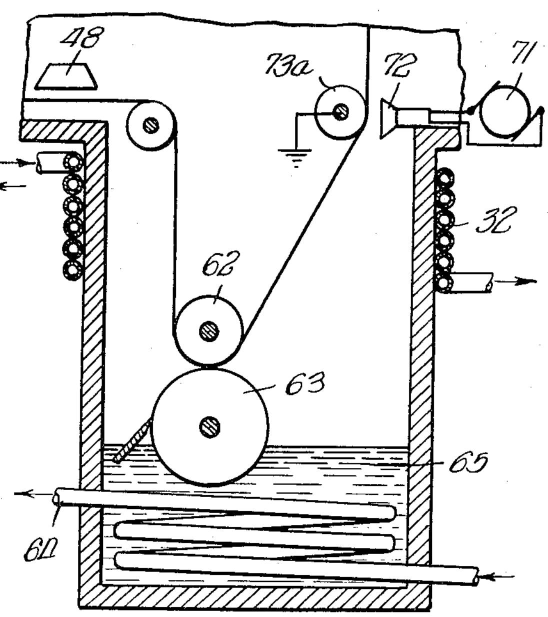
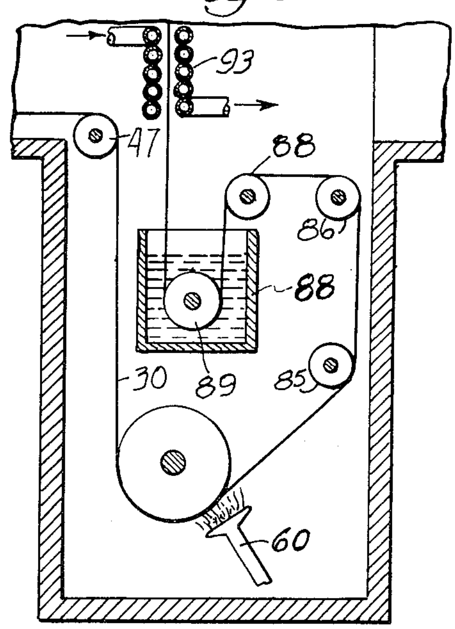


Fig. 8



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PRINTING AND COATING METHOD

Original Filed May 14, 1965

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Fig. 6

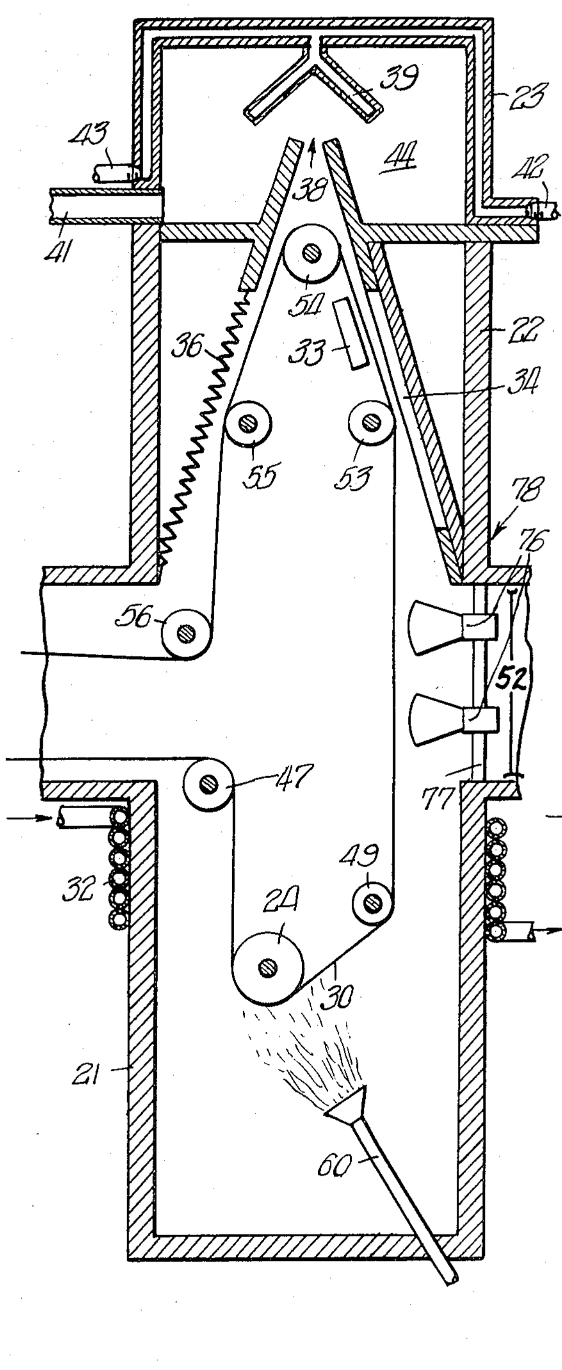
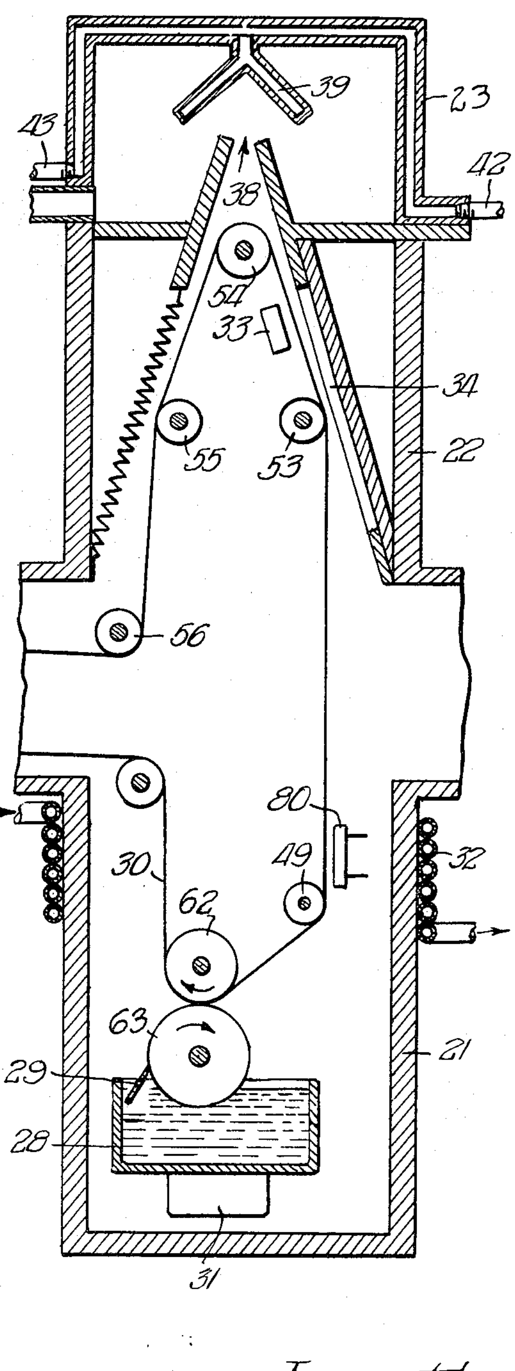


Fig. 7



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United States Patent Office 3,669,720
Patented June 13, 1972

3,669,720

PRINTING AND COATING METHOD

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Original application May 14, 1965, Ser. No. 455,936. Divided and this application June 25, 1969, Ser. No. 850,292
Int. Cl. B44d 1/44
U.S. Cl. 117—93.31 5 Claims

ABSTRACT OF THE DISCLOSURE

A method 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 ultrasonic irradiation for facilitating vaporization of the solvent constituent in the formulation and/or polymerization and crosslinking within the coating component while on the web or object surface.

BACKGROUND AND DESCRIPTION OF INVENTION

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

The present invention relates to printing and coating methods and apparatus. More particularly, this invention is concerned with improvements and innovations in methods of and apparatus for continuously printing or coating in a non-flammable atmosphere a travelling web or object surface by depositing thereon a suitable ink or coating composition dispersed or dissolved in a heavy solvent vehicle followed by in-line treatment 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 method and apparatus of the present invention, it is possible to accomplish high speed coating and printing of paper, plastic films, metal foils, textile fabrics, netting, non-woven 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 method and 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 method and apparatus of the present invention are particularly attractive commercially since they enable 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 method of and 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 a method and apparatus for continuously printing or coating a web or object surface in a non-flammable 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 method of and apparatus for continuously coating a fast travelling 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 method of and 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 a method of and 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 a method of and 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 method of and 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 in-line 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 method of and 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 in-line 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 method of and 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 method of and 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 is 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 method of and 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 a method of and 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 o fa 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 formualtion 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 from 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 facilatate 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 travelling 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 nonporous webs, such as metal foils, the heating element **34** is advantageously positioned on the coated side of the travelling web **30**. In some operations it is desirable to simultaneously heat both sides of the travelling 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 liquified solvent and returns it to a storage vessel (not shown) where it is mixed with make-up 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 patent, 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 **47***a* and **47***b* 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.) rubber-like 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 silicon 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 cycles per second. 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 **54**. 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**, **55** and **56** to a wind-up roller (not illustrated). With the present invention wind-up is not necessary since the travelling 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 rollers **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 July 17, 1961 and in my previously referred to patent, 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, trichloroxylene, 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% to 60% solids as compared to conventional ink or coating compositions wherein the solid content does not exceed 25% by weight.

The flurinated, 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 advantage of permitting deposit of the coating or ink composhition 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 non-combustible, 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 non-vacuum 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, hydrophillic coatings can be changed to oleophilliccoatings 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 than 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 Patent 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 over-all printing surface or it may carry a design whereon there are printing areas and non-printing 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 Patent 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% of diphenyl oxide having a boiling point of 258° C.). While not shown, a coil **32** such as shown in FIGS. 1 and 2 may also be provided.

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 make-up 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 ($\frac{1}{16}$") 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 an electrostatic 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, carnuba 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 physical 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 hydrophilic 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. Dielectricially covered treater roll **73***a*, 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 icnlude methylene dichloride, perchloroethylene, trichloroethylene, Chlorotene NU (Dow), pentachloroethylene, ethylene dichloride, trichloromethane, dichloromethane, trichlorotrifluoroethane, trichloromonofluoroethane and hexane, and various mixtures thereof. Aqueous solvents and diphase 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 (Klusel, Hercules Powder Co.), methyl cellulose, collagen and other proteinatious matter. These materials are soluble in the fluorinated and chlorinated solvent and can be applied in very thin films to the substrate surfaces. When subjected 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 founation 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 infra-red 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 **93** 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:

	Parts by weight
Sodium carbonate	40
Hexamethylenediamine	22
Water	500

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:

	Parts by volume
Sebacoyl chloride	15
Methylene chloride	500

The temperature of fountain **28** is maintained at about 70° F. with a web speed ranging from 100 to 2000 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 3200 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 4000 ml. To the above solution, 2000 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 (Klusel—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 gasket material receives two separate coatings applied in separate or continuous steps.

The first adhesive formulation is prepared from the following ingredients:

	Parts by weight
Diethylcyclohexylamine (amine catalyst)	50
Methylene chloride	50

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 2000 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:

100 parts by weight of Vorite 101 caster based polyester prepolymer (Baker Castor Oil Co.)

10 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 ultimatelv is stamped into a closure cap.

EXAMPLE IV

The present example is directed to a method of preparing micro-fine 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:

	Pts. by wt.
Molybdenum disulfide	10
Micro-size glass fibres (fiber glass)	5
"Teflon" micron size fibres	5
"Hycar" 1432 acrylic ester copolymer (B. F. Goodrich)	10
Chlorothene NU (Dow Chemical Co., Midland, Mich.)	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 resinated 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 advatageously used to collect and condense the solvent vapors. When dried the resinated pigment particles can be shipped or stored for subsequent use.

The olephillic 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.), polyethylene sperical micron beads, micro glass beads, boron micron fibers, tungsten disulfide, molybdenum selenide, tungsten selenide, graphite "Teflon" micron size fluorocarbon powder, anthracene, micron size "nylon" polycaprolactum heat stabilized powder, tetraethyl lead, di-n-butyltin sulfide and molybdenum xanthate.

EXAMPLE V

This example is directed to the coating of textile, paper, plastic and metal webs or object 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:

	Pts. by wt.
Silicone dimethylpolysiloxane polymer	20
Chlorothene NU (Dow Chemical Co., Midland Mich.)	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 travelling web, each being of 2200 to 2800 angstron units, are used with a web speed of 100 to 3000 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 expoxy-polyamide resin coatings to webs and object surfaces.

EXAMPLE VI

This example relates to a method of treating "non-printable" surfaces with a polymerizable coating formulation that acts as a good receptive surface for ink and coating deposits. Examples of the "non-printable" 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:

	Pts. by wt.
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 VII

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:

	Pts. by wt.
"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° F. to 70° F. The preferred temperature for depositing this formulation as a coating or ink onto the travelling 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 million electron 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 form of barium or cadmium sulfide, promethium 147 in the form of promethium 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 VIII

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:

	Pts. by wt.
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 IX

The present example is directed to the manufacture of novel electro-luminescent 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 electro-luminescent 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 electro-luminescent coating is applied. This coating is prepared from the following ingredients:

	Pts. by wt.
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, "Mylar" (E. I. du Pont) a polyester plastic film, polyvinyl fluoride, polyproxylene, polytetrafluoroethylene and polytrifluorochloroethylene.

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

	Pts. by wt.
Stannous tin chloride	10
Toluene sulfonic acid	10
An azeotropic mixture composed of 43% perchloroethylene 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:

	Pts. by wt.
7,7,8,8-tetraacyanoquinodimethan	20
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 X

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:

	Pts. by wt.
Crude crystal violet carbinol	80
Unoxidized hemotoxylin (logwood)	50
Methylene chloride	1000
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 characteristic of producing a jet black stain with a strong violet tone when contacted with a tannic acid-metallic salt.

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

	Pts. by wt.
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-Carboxyphenyl)Xanthene rhodamine-B-N-phenylactam and 3,3,bis(P-dimethylaminophenol)4,5,6,7 tetrachlorophthalide 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 ingredients:

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

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 of 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 XI

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:

	Pts. by wt.
Polawax A 31 (Croda Co., N.Y., a mon-ionic emulsifying wax)	3.5
Methylene chloride	51.9
Propylene glycol	6.0
"Gentron 11" (Allied Chemical Co., trichloromonofluoromethane)	4.0
Distilled water	33.6
Polyvinyl pyrrolidone	10.0
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, hydrolizable 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 XII

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

A typical formulation includes the following ingredients:

	Pts. by wt.
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% to 30% 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 bue, 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, CO_2 or N_2 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 numeral **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 oleophillic properties.

EXAMPLE XIII

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:

	Pts. by wt.
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 heterogenous 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 maye 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 film-like 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. The method of coating a web surface with a coating formulation which includes a chlorinated solvent, comprising the steps of
   depositing said coating formulation on the web surface,
   treating said coated web with high frequency sound waves for promoting solvent release of said coating formulation from said coated web surface,
   heating the chlorinated solvent component of said coating formulation to its boiling point to promote vaporization of said chlorinated solvent, and
   collecting and condensing said vaporized chlorinated solvent vapors.

2. The method of claim **1** wherein said formulation is deposited on such web surface at a temperature no higher than 70° F.

3. The method of claim **1** wherein said formulation is deposited on said web at a temperature no higher than 32° F.

4. The method of claim **1** wherein said coating formulation includes a chlorinated-fluorinated solvent.

5. The method of claim **1** wherein said high frequency sound waves are between 20,000 and 30,000 cycles per second.

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