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PRINTING PROCESS AND INK THEREFOR

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The present invention relates in general to ornamentation of the surface type and in particular to a process of printing designs on non-fibrous organic pellicles, especially of the water-swelling type, and to an ink composition which is capable of use in the printing operation and an article of manufacture produced by the process.

In the printing of non-fibrous pellicles heretofore, two types of ink have been employed. The first has been of the so-called "flash drying" type which has enabled the pellicles to be rapidly printed and stacked one on top of the other without smearing, but this type of ink has not been capable of tightly anchoring itself to the pellicles so that it could withstand immersion in water for any substantial length of time without separating from the pellicle. The second type of ink has been of the water-resistant type which is capable of anchoring itself to the pellicles so as to remain attached when the same is immersed in water, but this type has always been slow drying which has made it impossible to print continuously or to stack printed pellicles one on top of the other or to permit the printed surfaces of the pellicles to come in contact with any other object for several hours following printing. This has necessitated printing the pellicles in separate sheets or short pieces and the use of separators, commonly called "slip-sheets," between the sheets or pieces if they were stacked one on top of the other to prevent the printed surfaces from smearing or off-setting. Such printing procedures have been slow and consequently expensive.

It is a general object of the present invention to provide a process of printing pellicles.

It is a specific object of the present invention to provide a process of printing water-swelling, non-fibrous pellicles with a quick-drying ink to give a deposit which is immediately non-tacky and is also adherent when the printed pellicle is immersed in water.

It is a further object of the present invention to provide an ink which is quick-drying and capable of producing a deposit which is non-tacky and capable of adhering tenaciously to a water-swelling pellicle when the same is immersed in water as well as when it is subsequently dried.

It is a still further object of the present invention to provide an ink which is quick-drying and which after a short period will tenaciously adhere to a water-swelling pellicle when the same is immersed in water as well as when it is subsequently dried.

It is still another object of the present invention to provide an article of manufacture in the form of a water-swelling non-fibrous pellicle provided with a printed area or areas which will adhere to the pellicle during submersion of the same in water and during and after subsequent drying.

Other objects of the invention will in part be obvious and will in part be pointed out in the following detailed description.

In accordance with the present invention a non-tacky and strongly adherent design is produced on plasticized non-fibrous pellicles, preferably of the water swelling type, by printing the dry surface thereof with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a quantity of a hard resin sufficient to give a non-tacky ink deposit upon the evaporation of the ink vehicle, a coloring matter and a volatile organic vehicle for the ink, and evaporating the vehicle to form a non-tacky deposit and ageing the printed pellicle to harden the film-forming base whereby the ink deposit is rendered strongly adherent to the pellicle.

The present invention is particularly adapted for the continuous printing of designs on elongated articles such as continuous web, bands, tubings and the like formed of nonfibrous organic plastic materials. The designs may be formed on the surface of the dry pellicle by any suitable printing method such as typography or intaglio process and, if desired, the printing process may be carried out on a continuously operated printing press such as a rotary press. The printed material is then treated to evaporate the ink solvent and finally wound upon a suitable roller or severed into desired lengths. The printed pellicle is then aged, for example, for a period of twenty-four hours or longer to harden the drying oil or synthetic resin having drying characteristics. After the ink base has hardened, the ink deposit will adhere tenaciously to the pellicle when it is immersed in water as well as when the pellicle is later dried.

The invention accordingly comprises the several steps and relation of one or more of such steps with respect to each of the others, and the composition of matter and article possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

Pellicles which may be advantageously ornamented in accordance with the present invention may be formed of non-fibrous organic plastic material such as a non-fibrous cellulosic material, for example, cellulose hydrate regenerated from

viscose or cuprammonium cellulose or formed by de-esterifying cellulose esters; cellulose esters, such as cellulose acetate; or cellulose ethers, such as alkyl or hydroxy-alkyl cellulose ethers; also mixed esters, mixed ethers and ether-esters of cellulose. The pellicles may also be formed of casein, gelatine, water-swelling synthetic resins and other similar film-forming materials. The pellicles may be formed in any suitable manner as by casting, molding, coating, etc. A type of pellicle which is especially applicable for use with the present invention is plasticized cellulose hydrate, commonly known as "Cellophane".

The pellicles may be plasticized with any well known type of plasticizer depending upon the nature of the pellicle. It is preferred, however, that the pellicles be plasticized with one of the following materials: glycerol, sorbitol, sugar solutions, the glycols such as diethylene glycol, or a suitable mixture of these substances.

To condition the surface of the pellicle for printing, the plasticized pellicle is either completely dried to the condition of the dried articles of commerce, or the superficial parts of the plasticized pellicle are dried so that the surface is non-tacky and free of any liquid which will interfere with the wetting of the pellicle by the ink, or which will detract from the adherence of the ink deposit. In other words, the surface of the pellicle at the time of printing should be free of liquid and in a dry state although the interior of the pellicle need not be fully dried.

For the ink base employed in the present invention there is used a film-forming ink base selected from the group consisting of drying oils and synthetic resins having drying characteristics. Among the drying oils which may be employed are linseed oil, China-wood or tung oil, Perilla oil, poppy oil, menhaden oil, sardine oil, and synthetic oils of an ester formed by the reaction of glycerin and an unsaturated fatty acid, for example, an ester sold under the trade name "Neo-Fat," etc. and combinations of such oils.

The treatment of the oil to make it rapidly drying does not form an essential part of this invention since rapid drying oils are commonly known and may be prepared by heat treatment such as boiling or by blowing air through the oil or by adding commercial driers (siccatives) to the oil to increase its rate of oxidation or polymerization.

For the synthetic resins having drying characteristics there may be employed any oil modified synthetic resin, such for example as alkyd resins, phenol formaldehyde resins, glyptal resins, and the like, and mixtures of such resins, which have been formed in the presence of drying oils as is well known in the art. The resulting oil modified resin has drying characteristics similar to the drying oils above mentioned and for the purpose of the invention may be considered equivalent to the drying oil. However, the oil modified resins having drying characteristics should not be confused with the synthetic resins produced in the absence of drying oils and which do not have drying characteristics. The oil modified synthetic resins having drying characteristics are capable of forming hard, non-tacky films upon ageing and the drying rate of such resins may be accelerated by the use of commercial driers (siccatives) as is well known in the art. The invention contemplates also an ink base comprising a mixture of one or more drying oils with one or more synthetic resins having drying characteristics.

To facilitate the drying of the ink base, that is the evaporation of the drying oil or of the synthetic resin having drying characteristics, there is preferably employed in the ink a commercial drier or siccative. Such agents are oxidizing substances which when added to the ink hasten the hardening of the ink base. Among the siccatives which may be employed are resinates of lead, manganese, zinc, cobalt and/or manganese borate, cobalt linoleate, oleate dioxide, and the like. The amount of siccative to be added will depend upon the particular drying oil or synthetic resin employed and the rate of hardening desired. For the resin employed to render the ink deposit immediately non-tacky upon the evaporation of the volatile solvent there may be used either a natural or synthetic hard resin. Among the natural resins which are capable of use in the present invention are copal, shellac and ester gum.

Among the synthetic resins are glyptal resin, such as that sold under the trade name "Beckapol" or "Beckacite," polymerized acrylic acid and its derivatives, phenol condensate resin, such as that sold under the trade name "Amberol," chlorinated biphenyl resins, such as those sold under the trade name "Aroclors," and coumarone resins, such as those sold under the trade name "Cumar."

If desired, suitable unsaponifiable waxy or greasy materials, such as paraffin and/or petroleum jelly may be added to the above ingredients as well as spar varnish and suitable thickeners, such as a water soluble cellulose ether, starch and dextrine. The unsaponifiable waxy or greasy material tends to render the ink additionally resistant to water, the spar varnish enhances the adhesive qualities of the ink and the thickener provides a convenient material for controlling the consistency of the ink. In addition there may be added to the ink a hard wax such as montan or carnauba or synthetic hard waxes such as the product sold under the trade name "Halowax." The hard wax tends to render the ink deposit less tacky and imparts to the design a desirable surface gloss. The natural and synthetic hard resins and/or the hard wax serve as tack-reducing agents.

The ink may be compounded with or without coloring matter. If coloring matter is desired there may be employed any suitable inorganic pigment, such for example as lithopone, titanium dioxide, antimony oxide, whiting, lamp black and the like, or organic pigments, such for example as Prussian blue, ultramarine blue, Chinese blue, and the like, and/or any suitable dyestuffs as are well known in the art. The ink may contain also wetting agents, dispersion agents and thickening agents as well known in the art.

For printing all classes of non-fibrous organic plastic materials which must undergo changes in dimension during use, it is desirable to render the ink deposit sufficiently flexible to follow the changes in dimension of the base material. For this purpose there may be added to the ink composition a suitable plasticizer for the film-forming ink base such for example as castor oil, butyl stearate, dibutyl phthalate, ethyl lactate and the like.

For the liquid vehicle of the ink there may be employed a volatile organic solvent of the film-forming ink base which is preferably also a solvent of the hard resin and of the other solid ingredients. However, if the solvent of the film-forming ink base is not a solvent of the hard resin or of the other solid ingredients, additional spe-

cific volatile organic solvents for such other ingredients may be added to the ink base solvent. In addition there may be present in the liquid vehicle an organic liquid diluent which has a high volatility at the temperature used for evaporating the ink vehicle. At least one component of the liquid vehicle should be a liquid which wets the surface of the material to be printed. The ink base and/or resin solvents may be selected from the volatile aliphatic or aromatic hydrocarbons, lower alcohols, lower esters, ethers, and the like, for example, ethers of diethylene glycol (carbitol) or hydrogenated napthalene (tetralin). In the now preferred embodiment of the invention, the ink solvent comprises a mixture of toluene, butyl alcohol, and ethers of ethylene glycol, to which may be added suitable volatile diluents depending upon the particular ink composition.

The ink vehicle must be capable of being rapidly evaporated, that is flash dried, at temperatures which do not embrittle the non-fibrous material and leave the composition dry, hard and non-tacky. The general consideration is that the ink solvent must have a higher vapor pressure during drying than the vapor pressure of the mixture of plasticizer and water at the surface of the non-fibrous material. Since the water in the non-fibrous material is usually accompanied by a hygroscopic substance so as to form a plasticizer which is relatively non-volatile, the mixture is disposed to a large extent within the material so that surface evaporation is reduced to a minimum. It is possible therefore to subject the ink deposit on the surface of a plasticized water-swelling material to a heat source sufficient to raise the ink temperature above the boiling point of water without removing any appreciable amount of water from the printed material. It is consequently possible to use ink vehicles which are not substantially completely evaporated until the ink temperature reaches 150° C., but it is preferred that the aforementioned solvents be used. Accordingly, the freshly printed material is treated to evaporate the ink vehicle by exposing it to an air stream having a temperature of 80° to 90° C. for four or five minutes, or even at room temperature if the velocity of the drying air stream is increased. Alternately, the wet ink deposits may be flash dried by subjecting the ink deposits to a temperature of up to 150° C. for a few seconds as by passing a hot air blast rapidly over the material.

By way of explanation of the invention, but not by way of limitation the following will be given as a general range of ingredients suitable for use in the ink of the invention, the parts being by weight:

Film forming ink base	40 to 70
Hard resin	30 to 60
Siccative	0.02 to 0.1
Coloring matter as desired.	

By way of illustration, but not by way of limiting the invention the following specific examples of inks will be given, the parts being by weight:

	Example I	Example II
Bodied "Neo Fat" #19	50.0	
Tung oil		50.0
"Beckacite" 1111	50.0	50.0
Cobalt linoleate	0.1	0.1
Titanium dioxide	80.0	80.0
Tetralin	20.0	40.0
Carbitol	5.0	
Ethyl lactate	10.0	30.0

The ink of the present invention may be advantageously used to ornament the surfaces of water-swelling materials by using it to print the surfaces with designs, configurations, solid or mixed colors, pictorial illustrations and the like.

The use of a hard resin and a flash drying solvent in this manner in an oil base combines all of the advantages of an oil base ink on the one hand and of a flash-drying ink on the other hand without the disadvantages heretofore encountered with each. Therefore, the present oil base ink combines the desirable properties of an oil base ink, specifically, adherence of the ink deposit to the cellulose during immersion in water, and a desirable property of the flash-dry ink in that the deposit is immediately track-free. Since the solvent is volatile at temperatures which do not deleteriously affect the non-fibrous material the ink is flash-drying which makes it possible to rapidly print non-fibrous pellicles without the use of slip sheets and with absolute freedom from danger of smearing or offsetting. Also, the oil base which has hitherto rendered the ink slow drying causes the ink to be resistant to water and enables the ink to tenaciously adhere to the non-fibrous material when immersed in water and dried. Pellicles so printed can be subjected to the rigorous treatment usually associated with meat cooking and curing processes without affecting the printing.

The ink of the present invention is capable of extensive application since non-fibrous pellicles are frequently subjected to conditions which make it impossible to use inks hitherto known. For example, container closures such as those frequently used on liquor, perfume and medicine bottles, are customarily soaked in water or some other swelling medium prior to their application to containers. After they have been applied over the openings of containers, they are permitted to dry and shrink into tight contact with the container. It is, of course, necessary that printing inks used on such articles be capable of tenaciously adhering to the non-fibrous material throughout the entire process of application in order that it will be legible and attractive. It is also necessary that such articles be produced at a rapid rate in order to prevent their becoming prohibitively expensive. The contrast is apparent between such tedious and expensive printing operations and the printing operations which can be performed with the ink of the present invention wherein non-fibrous material may be printed in continuous lengths and immediately wound into rolls or severed and stacked one upon another so as to require a very small storage space. Since the period over which the ink deposit becomes resistant to water is short, being in the neighborhood of twenty-four hours, the amount of storage space is further reduced to an absolute minimum and a waiting period between the printing of the non-fibrous material and the ultimate use of the material is practically eliminated since this period can be used to ship or otherwise deliver the printed non-fibrous material to the points at which it is to be applied to containers, used as meat or other food containers, etc.

The invention is particularly applicable for the printing of designs on endless tubing adapted to be used as sausage casings. Such tubings may be formed of cellulose hydrate regenerated from viscose or by the deesterification of nitrocellulose and the like. To prepare the tubing for printing,

it is softened and dried in the usual manner to produce a commercially dried product and the dried tubing is then printed with the ink of the invention and the liquid vehicle evaporated by flash drying as above described. The flash dried ink deposits are immediately non-tacky and the tubing may be rolled upon itself. The printed material is then aged for a short period of time, about three to four days, during which the film-forming oil base hardens and renders the ink deposit strongly adherent and resistant to peeling in the presence of water as during the soaking of the casings and the cooking of the sausage.

In the printing of endless tubing which is to be cut transversely into short bands for use as container closures it is necessary to prevent the irreversible shrinkage on drying of the material so that the printed material will retain its tendency to swell in water and shrink again upon drying as is necessary when the band is used as a shrinkable container closure. To maintain the shrinking characteristics the tubing is taken in the gel state before drying and plasticized with a large quantity of a water soluble plasticizer such as glucose, sorbitol, diethylene glycol, or the like, and then dried carefully to produce a liquid free surface, but not to completely dehydrate the material. After the printing of the tubing and the ageing of the ink deposit, the tubing may be soaked in water whereupon the plasticizer is dissolved out and water is imbibed by the tubing. The swollen tubing will be found to have substantially the same swelling and shrinking characteristics as the original tubing in the gel state.

Since certain changes in carrying out the above processes and certain modifications in the article and composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the foregoing description shall be interpreted as illustrative and not in a limiting sense.

The invention having been described, what is claimed is:

1. In a process of surface ornamentation of a pellicle formed of non-fibrous organic material by printing, the steps comprising printing a design on the surface of the pellicle with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, evaporating the ink vehicle and ageing the printed pellicle to harden the film-forming base.

2. In a process of surface ornamentation of a pellicle formed of non-fibrous organic material by printing, the steps comprising printing a design on the surface of the pellicle with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a coloring matter, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, evaporating the ink vehicle and ageing the printed pellicle to harden the film-forming base.

3. In a process of surface ornamentation of a pellicle formed of non-fibrous organic material by printing, the steps comprising printing a design on the surface of the pellicle with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a siccative, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, evaporating the ink vehicle and ageing the printed pellicle to harden the film-forming base.

4. In a process of surface ornamentation of a pellicle formed of non-fibrous organic material by printing, the steps comprising printing a design on the surface of the pellicle with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a coloring matter, a siccative, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, evaporating the ink vehicle and ageing the printed pellicle to harden the film-forming base.

5. In a process of surface ornamentation of a pellicle formed of non-fibrous organic material by printing, the steps comprising printing a design on the surface of the pellicle with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, flash-drying the ink deposit, and ageing the printed pellicle until the ink base has hardened.

6. In a process of printing sausage casings formed of non-fibrous organic material comprising, drying the surface of the casing and printing a design on the dry surface with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, evaporating the ink vehicle and ageing the printed casing to harden the film-forming base.

7. In a process of printing a shrinkable container closure formed of a non-fibrous organic material comprising plasticizing the closure, drying the surface of the closure, printing on the dry surface with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle, evaporating the ink vehicle and aging the printed closure to harden the film-forming base.

8. A printing ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle.

9. A printing ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a coloring matter, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle.

10. A printing ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a siccative, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle.

11. A printing ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying charac-

teristics, a coloring matter, a siccative, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle.

12. A printing ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics in an amount of from 40 to 70 parts by weight, a hard resin in an amount of from 30 to 60 parts, and a flash-drying vehicle for the ink, the resin rendering the ink deposit non-tacky upon evaporation of the vehicle.

13. An ink for printing films, sheets, bands or tubing formed of non-fibrous organic material comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a hard resin to give a non-tacky ink deposit upon the evaporation of the vehicle.

14. In a process of surface ornamentation by printing, the steps comprising printing a design on the surface of a pellicle with an ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a tack-reducing agent to render the ink deposit non-tacky upon the evaporation of the vehicle, evaporating the ink vehicle and ageing the printed pellicle to harden the film-forming base.

15. A printing ink comprising a film-forming base selected from the group consisting of drying oils and synthetic resins having drying characteristics, a flash-drying vehicle for the ink, and a tack-reducing agent to render the ink deposit non-tacky upon the evaporation of the vehicle.

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