

UNITED STATES PATENT OFFICE

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PREPARATION OF PHOTOSSETTING
COATING COMPOSITIONGerald L. Wendt, New York, N. Y., assignor to
Sun Chemical Corporation, a corporation of
DelawareNo Drawing. Original application April 27, 1944,
Serial No. 533,060. Divided and this applica-
tion August 21, 1946, Serial No. 692,151

8 Claims. (Cl. 204-161)

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This invention relates to the preparation of coating and impregnating compositions containing eleostearin, to the compositions so prepared, and to methods for rapidly drying or setting these compositions.

While there are many industries in which quick-drying coating or impregnating compositions are desirable, the printing industry is one in which such compositions are of great importance. Modern high speed press operations require inks which will dry quickly enough to avoid the difficulties of smudging, smearing and offsetting. Printing at these high speeds has been made possible by a number of developments, such as by modifying the composition of the inks or the character of the surface to be printed upon, by heating the printed webs or sheets, or by other means. The present invention therefore is particularly applicable in the printing industry, although it is not limited thereto and may be used in other fields where rapidly drying coating or impregnating compositions are desired—as in paints, varnishes, and the like.

This application is a division of applicant's pending application Serial No. 533,060, filed April 27, 1944, which has become abandoned, which in turn is a continuation of applicant's earlier filed application Serial No. 266,682, filed April 7, 1939, which has become abandoned.

Illustrative of the need for rapid drying or setting of the printed impression to non-offsetting condition before contact with a surface which can cause offsetting or smearing or smudging are the speeds of the traveling paper webs in present day high speed printing operations. These web speeds range for example from 300 to 1800 feet per minute. Hence procedures have been adopted for drying in a very short time—say 3 or 4 seconds or less, and even down to fractions of a second. Because if an ink were used which required say 10 seconds to dry or set up sufficiently so that it would not offset, smear or smudge, the web would have to travel 50 to 300 feet before contacting its printed face in offsetting relation with any object, e. g. before making a second impression or contacting with a smearing or smudging part of the press mechanism, or before backing up, re-winding, stacking, etc.

Ordinarily the time required for a printing ink to set up sufficiently to avoid offsetting is definitely less than the time required for complete drying or setting of the same ink. Again, the conditions which contribute toward offsetting vary more or less—that is to say, the amount of offsetting, smearing or smudging, of any given ink

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at any given point in its drying obviously depends upon the amount of pressure, slipping action, or the like applied to the ink impression.

It is therefore an object of the present invention to provide coating and impregnating compositions which can under proper photosetting conditions be dried or set up rapidly to be non-offsetting and non-smudging.

Another object is to provide such proper conditions for effecting rapid drying or setting of these compositions.

Another object is to provide inks, and means for setting them with sufficient rapidity, which are particularly useful for high speed printing purposes.

Other objects will be evident from the present disclosure.

In the practicing of the present invention, compositions are prepared which comprise as an essential a substance made up largely or wholly of eleostearin or keto eleostearin, and the said compositions also include such binders, pigments, solvent, or other materials as may be required to make them suitable for the use desired. The present invention comprises, briefly, the preparation of a suitable composition of such kind which is essentially responsive to light of certain limited wave lengths of such range as to photoset with the required and desired rapidity to give non-offsetting or non-smudging or non-smearing condition as stated; taking suitable steps to accelerate appreciably the rapid set-up or drying of said composition under photosetting conditions subsequent to applying it to the object to be coated, impregnated, or impressed; coating, impregnating or impressing the object with the composition; and then subjecting the resulting object to light of suitable wave length, with or without other accelerating means, to photoset rapidly the coating or impregnation.

It is found, in accordance with the present invention, that eleostearin and keto eleostearin are particularly susceptible to rapid photosetting under the influence of, or irradiation by, certain definite wave length bands of radiation which are severally in the ultraviolet region. The speed of this photosetting can be markedly accelerated by various means, as by adding promoters or by removing inhibitors, or both, as will be discussed in greater detail below.

Eleostearin is a natural product, which is the glyceryl ester of eleostearic acid. It is found naturally, in the alpha form (i. e. as tri- α -eleostearin), in tung oil, and constitutes about 85 to 90% thereof. A small amount of the beta isomer is

present in eleostearin and may be made from the alpha isomer; and it is a solid. Both isomers are suitable for use in the present invention, and both are included herein under the term "eleostearin."

Keto eleostearin is eleostearin in which all of the radicals of eleostearic acid are replaced by radicals of 4-keto eleostearic acid (licanic acid). These radicals are also known as the eleostearate radicals and the 4-keto eleostearate or licanate radical respectively. Oiticica oil is largely keto eleostearin.

There are three conjugated double bonds in each of the acid radicals of eleostearin and keto eleostearin. This configuration is potentially extremely reactive and I have found that when initiated and effected by the procedure of the present invention the drying of either eleostearin or keto eleostearin proceeds very rapidly to form a solid three-dimensional molecular structure. In this manner the eleostearin-containing compositions of this invention are rapidly set or dried. For convenience, therefore, the term "eleostearin" herein will include not only the isomers, as above stated, but keto eleostearin as well. The term "eleostearin" is also intended to include herein other closely related compounds of eleostearic acid or keto eleostearic acid which are characterized by containing at least two radicals of one or the other of these acids. Thus, esters of these acids with polyhydric alcohols (of which glycerine is one) are included.

This rapid setting or drying is effected, as already stated, by the combined action of the accelerating means and of radiation of suitable wave lengths within the ultraviolet range.

While it is known that radiations within the ultraviolet and within the infrared ranges, as well as visible radiations, may have some physical or chemical effects upon various materials, including some oils used in inks; no one before has known, as I have discovered, that waves within each of two, mutually exclusive, comparatively narrow wave bands and each of which is within the ultraviolet range, are particularly specific, but differently so, to effectuate rapid setting of ink materials containing the type of conjugated double bond system in eleostearin. One of these specific bands is the range of waves within 2450-2600 Å. and the other is within the 2800-3500 Å. range, and the specific and particular effectiveness of these two mutually exclusive, comparatively narrow wave bands, in the ultraviolet range, are both disclosed and claimed in my said copending application S. N. 533,060, and the companion application Serial No. 692,150, filed of even date herewith as a division of said application S. N. 533,060 relates more particularly to my invention with respect to the particular band of waves within the range 2800-3500 Å.; while the instant application, which is also a division of my said application S. N. 533,060, relates more particularly to my invention with respect to the particular band of waves within the range 2450-2600 Å.

The range 2450-2600 Å. appears to be specific to ink materials having the type of conjugated double bond system in eleostearin when used to the exclusion of objectionable waves outside said band and particularly to the exclusion of waves within the band 2800-3500 Å., as set out in said copending application S. N. 533,060 and in my companion application filed of even date herewith as a division thereof and hereinabove re-

ferred to; while the range 2800-3500 Å. is likewise specific in its own different way to ink materials having the type of conjugated double bond system in eleostearin, when used to the exclusion of objectionable waves outside said particular band and within the ultraviolet range, and particularly to the exclusion of waves within the other specific band or range of 2450-2600 Å., to which this instant application relates. The products which result from the use of said 2800-3500 Å. wave band have a smooth, glossy surface; while, in contrast if waves within the band 2450-2600 Å. of the instant invention are used the products which result have a dull or matte surface on the dried oil.

While I am not sure as to why the use of each of these two mutually exclusive and comparatively narrow wave bands, free from objectionable waves within the ultraviolet range (which as stated is understood to include waves from about 2000 Å., below which substantially all of the radiations would be absorbed by the air, and up to approximately 4000 Å., these limits depending for example upon the hazy or other radiation absorbing conditions of the air, which latter marks approximately the dividing zone between the ultraviolet and the visible radiations) I have found nevertheless that each of these two wave bands, when free from objectionable inhibiting quantities of waves within the ultraviolet range and outside the specific narrow band being used, and particularly when substantially free from waves within the other specified and mutually exclusive band, will have a very unusual and unexpected specific effect particularly upon materials having the characteristics such as the conjugated double bond system of eleostearin.

In accordance with the invention of the present divisional application, therefore, I have found, as stated above, that radiation within the range of 2450-2600 Å., and with the waves within such 2450-2600 Å. band applied for the setting operation while substantially free of the mutually exclusive waves of the other specified band and free from objectionable quantities of other waves in the ultraviolet range, is particularly effective in causing rapid setting of such ink materials, containing selectively responsive constituent, such as eleostearin, to produce rapidly set imprints which have a dried oil film with the dull or matte surface referred to.

Acceleration of the photosetting action of waves in this 2450-2600 Å. band may be effected by the use of promoters or by the removal of inhibitors, or both. The degree or extent of acceleration will of course depend upon many factors, such as the type and quantity of promoters used, but I prefer to employ accelerating means which will reduce by at least 25%, and preferably by at least 50%, the time required for photosetting under otherwise identical conditions.

Types of compounds suitable for promoters of the photosetting of eleostearin under the conditions of the present invention are those which are influenced by ultraviolet radiation to activate or release active Br, I, and/or O.

One such type of promoter is blown eleostearin, which is conveniently available in the form of blown tung oil or blown oiticica oil. Blowing of these oils results in the loss of some of the double bonds (i. e. in some loss of unsaturation) due to union with oxygen, probably including the formation of peroxides, together with some polymerization. This blowing may be carried out to a

greater or less extent, as desired—that is, the eleostearin may be only partly blown. As is well known, these oils may be bodied by heat alone; however, a different product results from that obtained by blowing. This resulting heat-bodied product has undergone extensive polymerization, without the formation of compounds with oxygen, and is definitely unsuited for use in the present process.

Alternatively, I may use an extraneous promoter having the foregoing characteristic of activating or releasing active Br, I, and/or O under the conditions imposed. Typical of such promoters are the bromine, iodine, and nitro derivatives of methane wherein at least three of the carbon bonds are attached to active groups, e. g. bromoform, bromal, iodoform, carbon tetrabromide, and tetranitromethane. Also useful are some other halogen-containing compounds such as heptachloropropane and hexachlorophenol, and certain iodonium compounds and substances which are easily converted thereinto, e. g., iodosobenzene and phenyl iodonium chloride. I have found that the addition of promoters of this type to raw eleostearin accelerates quick setting as much as does the blowing of the eleostearin—or even more, if enough of such promoters is used. They may also be used to promote the setting of blown eleostearin.

A few of these extraneous promoters are so reactive that they will cause the eleostearin compositions containing them to set up even on standing in the dark. Of those listed above, tetranitromethane is such a promoter. Tetranitromethane is more or less unstable and hence care should be taken to avoid explosive conditions. Hence such promoters as tetranitromethane would not be used when the composition is to be kept for any length of time before use. Such promoters are, however, entirely suitable if added to the composition immediately before use.

Alternatively to the procedure of adding extraneous promoters to the compositions containing eleostearin, it is possible to incorporate these promoters in the paper or other surface or article to be coated or impregnated, whereupon these promoters are effective as soon as the composition is applied to such surface or article, and subjected to radiation of appropriate limited wave lengths as described herein. In following this alternative procedure, however, consideration should be given to the fact that some of the promoters are relatively volatile.

Another method of accelerating the photosetting of tung and oiticica oils, which method may be used with or without the promoters, is to remove substances which inhibit the photosetting action. Tung and oiticica oils characteristically contain about 10 to 15% of substances other than eleostearin. More or less of these substances can be removed as by the method described below, and those having a vapor pressure above (i. e. a boiling point below) that of eleostearin appear to have an inhibiting effect on the photosetting. In other words, for example, I have found purified eleostearin more susceptible to the photosetting action by radiation of 2450–2600 Å. wave length than are the raw oils. The separation of these inhibitors from the raw oils may be performed in various ways. For example, it may be performed by distillation, but most ordinary methods of distillation are not suitable as they result either in decomposition of the oil, due to the high heat required for distillation even at the ordinary commercial range of low pressures,

or at least in heat-bodilying the oil, and hence in considerable polymerization without formation of oxygen-containing promoting agents, which, as already stated, is to be avoided prior to subjecting the composition to the desired wave length radiation. A suitable method of distillation is that known as “short-path molecular distillation,” wherein the oil is flowed in a thin film over a heated surface in a chamber under extremely high vacuum, and as the molecules vaporize, they pass quickly to a cooled surface situated a relatively short distance from the heated surface. It is not necessary nor even desirable to distill the eleostearin itself; the important point is to distill off the inhibitors having a higher vapor pressure (lower boiling point). This type of distillation has been recently introduced commercially for the separation of the constituents of more or less complex natural mixtures which would be damaged or destroyed by attempts to separate them by hitherto used distillation methods.

This procedure of removing inhibitors may be used in conjunction with promoters—promoters including both the blown eleostearin and the extraneous promoters such as carbon tetrabromide, etc. described above. Or it may be used without promoters. In ordinary commercial practice, elimination of inhibitors would not ordinarily be performed, because of the expense of doing so, although in some particular instances, as where an extremely rapid photosetting is desired, such procedure may be advantageously used in addition to the use of promoters.

As already stated, one of the preferred wave lengths of the radiation to effect rapid photosetting is 2450–2600 Å. The mercury spectrum line 2537 Å. falls in this region. However, most mercury vapor ultraviolet light sources now available commercially have, in addition, ultraviolet radiation of the following characteristic wave length bands: 3126–3132 Å.; 3650–3663 Å.; 4047–4078 Å.; 4339 Å., and 4347–4358 Å., and each of these bands is present in an intensity of about one to three times the intensity of the 2537 Å. line. There are also generally minor amounts of radiation at other wave lengths, but these amounts are as a rule less than 10% of the amount of 2537 Å.

Some special light sources, however, such as the cold discharge mercury vapor tube, have the bulk of the radiation at the 2537 Å. band; in the case of this cold discharge tube the total of the radiation intensities at other wave length bands, chiefly those mentioned above, is in the neighborhood of 15% of the total radiation, while that at 2537 Å. is about 85% of the total. The conventional hot mercury arcs above referred to, however, have only about 10% of their radiation at 2537 Å., the other 90% coming chiefly at the other bands as mentioned above. These hot arcs can be used to effect photosetting in accordance with the procedure of this invention, in a time comparable with that of the light sources which are largely in the 2537 Å. band if these hot arcs are operated to produce an intensity at the 2537 Å. band of several times (say 5 to 10 times) that of the cold discharge tube or other light source of similar characteristics, i. e., to approximate such radiation as is secured from the cold discharge mercury vapor tube, and if the detrimental radiation outside the 2450–2600 Å. range is sufficiently reduced as by use of a suitable filter, such as an aqueous solution of a soluble nitrate,

e. g., sodium or potassium nitrate. I therefore prefer to use light sources, such as the cold discharge mercury vapor tube, in which the radiation in the 2450-2600 Å. range is sufficiently larger than that in any other one band or range so that the effective amount of such 2450-2600 Å. radiation is at least about 50% of the total radiation from the light source.

This cold discharge tube referred to above typically contains a relatively very small amount of mercury, and may also contain some argon as a starter. Larger amounts of mercury, as in the usual hot arcs, result in considerable reabsorption (and hence weakening relative to other bands) of the 2537 Å. band.

The procedure of this invention may be conveniently carried out as follows: A composition of the type desired is made up, using tung or oiticica oil or mixtures thereof, together with such other materials as may be required—e. g., binders, solvents, other oils such as linseed, pigments, etc. Means for promoting the photosetting is effected, either by first blowing the tung or oiticica oil, or by adding an extraneous promoter of the type already described, or by removing inhibitors of photosetting—or by combinations of these. The composition is then applied to the object to be coated, impregnated or impressed—which object may be glazed or unglazed paper, or wood, cloth, glass, metal, synthetic resin sheets, regenerated cellulosic sheets, etc.—and the coated or impressed surface is subjected to a source of light rich in radiation in the 2450-2600 Å. range. The light source is placed as near as conveniently possible to the coated surface, and is preferably provided with a reflector to concentrate the light upon the surface. A distance of ½ inch to 5 inches between the surface and the light source may be used satisfactorily, for example.

Heated air may sometimes be used to advantage to hasten the drying. In place of heated air, the paper or other surface to be coated or impregnated may be heated; or both heated surface and heated air may be used. Driers, such as cobalt linoleate, mercury naphthenate, etc., may be used in the composition, if desired, to assist in the setting and drying.

As a modification of the present process, the eleostearin may be exposed in thin films to the action of radiation of the wave lengths preferred herein, prior to the application of the coating composition to the object and prior to the final photosetting operation. Such preliminary exposure is for the purpose of partially setting up the compositions, in order to accelerate the final photosetting action.

The following will serve as a specific example of the operation of the present invention, with particular attention to its use in connection with printing in high-speed press operations.

A black printing ink of the following formula is prepared, the parts being by weight:

	Parts
Raw tung oil -----	40.0
Gum varnish -----	22.5
Stearin pitch -----	5.5
Wax compound -----	3.0
Black pigment -----	17.0
Blue pigment -----	12.0
	100.0

The gum varnish, stearin pitch, and wax compound are conventional substances for making

printing inks, and serve their usual functions. Thus, the stearin pitch assists in controlling length and flow characteristics, and the wax compound reduces tendency to offset. The wax compound may be carnauba or other suitable wax dispersed in an oil such as linseed oil.

To 90 parts of the foregoing ink composition add 10 parts of promoter, e. g. carbon tetrabromide.

The ink so prepared is used for printing in high speed press operations in the usual manner. Then, as the paper leaves the printing means its printed surface is exposed to the radiation from a cold mercury discharge tube, or a bank of such tubes, with suitable reflecting means, so that substantially all the radiation from said tube or tubes falls on the printed surface. The radiation from these tubes is such that, for example, at least about 85% of it falls within the range of 2450-2600 Å., and principally at 2537 Å. By this procedure the ink is dried to non-offsetting condition in a very short time, ranging from about two seconds down to a small fraction of a second, when one tube is used. The exact time depends upon thickness of the printed impression, surface or finish of the paper, and severity of offset conditions, but under average working conditions the drying time to non-offsetting condition will be definitely less than one second. This time can also be shortened still further by having a plurality of tubes, so arranged that the printed impression is subjected successively to the radiation from each of these several tubes, for example. Thus each tube may extend transversely the entire width of the web, and have its radiation portion substantially coextensive with said width, and a series of two or more of these tubes, each with its own reflector and associated mechanism, may be placed at suitable intervals along the line of travel of the web. The distance between these intervals will obviously depend upon the speed of the web, characteristics of ink and paper, and other factors, and should therefore be determined for each particular set of conditions. The characteristics of some types of tubes may prevent their extending the full width of the web, hence in such instances a series of shorter tubes may be used, which series extends the full width of the web. But with irradiation with the selected wave band drying to non-offsetting or non-smudging condition may be attained within the speed range stated by coordinating the controlling factors as stated.

The amounts of the various ingredients given in the foregoing example may be varied considerably or replaced by others, in accordance with the characteristics desired in the composition. The raw tung oil may be replaced by oiticica oil; the amount used may be increased or decreased above or below the amount specified. However, it is preferable to use at least about 20% of raw or blown tung or oiticica oils or mixtures thereof, in order to give a composition which will photoset with sufficient rapidity under the conditions of the procedure of the present invention.

The amount of extraneous promoter may vary considerably, depending upon the nature of the promoter, the results desired, the time the ink must be kept before use, and the presence or absence of inhibitors and of inherent promoter (in the form of the blown oils). In the foregoing example, for instance, the amount of carbon tetrabromide or its equivalent may range between 1 and 20 parts per 100 parts of the ink base,

depending on the speed of drying or setting desired.

It is to be understood that the foregoing disclosure is for the purpose of illustration of the present invention, and that various changes and modifications may be made without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing as an essential ingredient not less than 20% of a compound having in its molecule at least two radicals of the group consisting of eleostearate and keto eleostearate and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50% within the wave length band 2450-2600 Å.

2. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing as essential ingredients not less than 20% of a compound having in its molecule at least two radicals of the group consisting of the eleostearate radical and the keto eleostearate radical, and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50% within the wave length band 2450-2600 Å., and to exclude any substantial proportion of any wave length of the band 2800-3500 Å.

3. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing a photosetting promoter and, as an essential ingredient, not less than 20 per cent of a compound having in its molecule at least two radicals of the group consisting of eleostearate and keto eleostearate and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50 per cent within the wave length band 2450-2600 Å.

4. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing as an essential ingredient not less than 20 per cent of a compound having in its molecule at least two radicals of the group consisting of eleostearate and keto eleostearate and from which compound a substantial amount of substances having vapor pressure above that of eleostearin have been removed and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50 per cent within the wave length band 2450-2600 Å.

5. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing a photosetting promoter and, as an essential ingredient, not less than 20 per cent of a compound having in its molecule at least two radicals of the group consisting of eleostearate and keto eleostearate and from which compound a substantial amount of substances having vapor pressure above that of eleostearin have been removed and subjecting such applied composition to radiation controlled

to contain essentially not less than approximately 50 per cent within the wave length band 2450-2600 Å.

6. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing a photosetting promoter and, as essential ingredients, not less than 20 per cent of a compound having in its molecule at least two radicals of the group consisting of the eleostearate radical and the keto eleostearate radical, and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50 per cent within the wave length band 2450-2600 Å., and to exclude any substantial proportion of any wave length of the band 2800-3500 Å.

7. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing as essential ingredients not less than 20 per cent of a compound having in its molecule at least two radicals of the group consisting of the eleostearate radical and the keto eleostearate radical, and from which compound a substantial amount of substances having vapor pressure above that of eleostearin have been removed and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50 per cent within the wave length band 2450-2600 Å., and to exclude any substantial proportion of any wave length of the band 2800-3500 Å.

8. Method of causing rapid setting of a coating composition which comprises applying a coating composition containing a photosetting promoter and, as essential ingredients not less than 20 per cent of a compound having in its molecule at least two radicals of the group consisting of the eleostearate radical and the keto eleostearate radical, and from which compound a substantial amount of substances having vapor pressure above that of eleostearin have been removed and subjecting such applied composition to radiation controlled to contain essentially not less than approximately 50 per cent within the wave length band 2450-2600 Å., and to exclude any substantial proportion of any wave length of the band 2800-3500 Å.

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