

UNITED STATES PATENT OFFICE

2,647,060

NONSMUDGING DUPLICATING INK

William N. B. Armstrong and Hyman S. Kredentser, Toronto, Ontario, Canada, assignors to Ontario Research Foundation, Toronto, Ontario, Canada

No Drawing. Application February 13, 1950,
Serial No. 144,036

3 Claims. (Cl. 106—26)

1

This invention relates to transfer or duplicating inks, and more particularly to a new and useful transfer or duplicating ink which can be applied in the same manner as ordinary printing inks on standard types of printing presses or the like.

In many different types of business forms it is desirable that the sheets contain on the reverse side throughout at least certain areas a transfer or carbon material as is well known in the manifolding art so that writing occurring in these areas is duplicated on an undersheet.

It is highly desirable that such business forms be "spot carbonized" as economically as possible and therefore desirable that the application of the transfer or carbon material be capable of being made by a printing press or the like.

To such end it has heretofore been proposed to apply the transfer material as a grease type ink such as a grease carbon ink. Such an ink while lending itself to a printing press contains ingredients such as linseed oil which causes premature or rapid hardening with a resulting loss of transfer properties on aging. Further this type of ink also has the disagreeable property of smudging.

It has also been proposed to apply the transfer material as a "hot-melt" wax-carbon ink. Such an ink does essentially eliminate smudging and maintains its transfer properties on aging. However, a certain amount of undesirable penetration is experienced when coating paper with this ink. Another disadvantage which is a serious one is that the ink must have a hot application requiring special equipment, heat, and a skilled operator to maintain the necessary controls of application.

As an improvement over the "hot melt" wax-carbon ink it has also been proposed to convey the transfer or carbon material to the paper in a cold application by means of a suitable volatile vehicle in which transfer and wax particles are suspended or dispersed but which does not dissolve the wax in an unheated state. However, to complete the formation of the transfer surface the printed area must be subsequently heat treated to cause the wax and/or the like to fuse and to drive off the unwanted volatile.

It is therefore the object of this invention to overcome the disadvantage of such previous proposals by providing a transfer or duplicating ink composition which can be applied in a cold application in the same manner as ordinary printing inks on standard types of printing presses without penetration of the paper to provide a

2

resultant film which will be non-smudging, have an excellent transfer property and will maintain its original transfer property after long-time aging.

This object is obtained by providing a novel transfer or duplicating ink composition in which the duplicating or transfer film forming constituents are carried to the paper by a non-penetrating quick drying solvent and are capable of drying almost instantaneously into a non-smudging, flexible transfer film with excellent transfer properties.

More specifically the principal feature of the invention resides in the provision of a transfer ink composition comprising a wax-oil-colour blend, a hardening agent in the form of a friable resin, a primary amide of a long chain fatty acid forming a thickening agent, a film forming agent, and a filler, dispersed in an organic solvent. A combination of the above ingredients can produce a transfer film which will be of sufficient hardness and flexibility, be non-smudging yet can be broken by the pressure of a pencil and will provide excellent transfer properties undiminished on aging. By a suitable choice of film forming ingredients and solvent the paper will not be penetrated and the distillation range can be chosen as such as to meet the particular application of the ink, for instance, application by doctor blade or application by a standard printing press so that the composition will have the requisite rate of drying, that is, the solvent will have the requisite rate of evaporation suitable for the method of application.

In most applications the ink composition desired is a carbon ink but it will be understood that the invention is applicable to and includes any transfer or duplicating ink affording cold solvent application in accordance with the teachings herein disclosed.

For a non-smudging carbon ink for duplicating paper compounded in accordance with this invention a suitable wax-oil-colour blend comprises a blend of waxes, a paraffin oil, pigments, dyes and a wetting agent for the pigments and a solvent for the dyes. Such a wax-oil-colour blend is common in the industry and this invention makes no claim to novelty of such a blend. An example of a suitable wax-oil-colour blend is a mixture of ouricury wax, paraffin wax (133–136° F. M. P.) Bareco (165° F. M. P.) Peerless Black, Static Black, ink oil, methyl violet, and oleic acid.

The functioning of each of the above ingredients is well understood in the art and further

particulars as to their functioning or to equivalent substitutes are not deemed necessary to the understanding of this invention.

First attempts at carrying such a wax-oil-colour blend to the paper by a cold solvent application included milling the mixture hot and dissolving it after milling in a solvent and adding a resin to harden the film and preventing smudging upon evaporation of the solvent or drying of the film. Such a composition however gave unsatisfactory results indicating that the highly desirable cold application of a transfer or duplicating ink was not feasible.

We have discovered however that if with the wax-oil-colour blend, and resin, a primary amide of a long chain fatty acid, a film forming agent of the nature of ethyl cellulose, and an inert pigment filler are combined they can be dissolved or dispersed in an active solvent or a blend of active solvent and a diluent of a suitable distillation range for the desired method of application and carried to the paper by cold application to have the same consistency and drying qualities as ordinary printing ink for application by a printing press, doctor blade or the like and providing upon drying a more desirable transfer film than has heretofore been possible. The film that is obtained according to our discovery is sufficiently hard and flexible to prevent smudging and cracking respectively and yet can readily be broken by the pressure of the pencil to provide an excellent transfer property which remains undiminished on long aging.

According to our invention a specific example of a non-smudging carbon ink for duplicating paper which retains its initial transfer properties on aging consists of:

Example I

	Parts by weight
Wax-oil-colour blend.....	126
Bentonite filler.....	30
Glycerol ester of hydrogenated rosin.....	26
A blend of primary amides of long-chain fatty acids ¹	26
Ethyl cellulose N-200.....	1.3
Aromatic petroleum solvent having a distillation range of 345° F. to 412° F.....	172

¹ A suitable amide blend consists of 25% hexadecanamide; 70% octadecanamide; and 5% octadecanamide.

The wax-oil-colour blend is milled with the bentonite in the above example and consists of:

	Parts by weight
Ouricury wax.....	27
Paraffin wax (125° F. to 128° F.).....	21
Microcrystalline wax (165° F.).....	5.25
High strength carbon black.....	27
Medium strength carbon black.....	15
Ink oil (a light paraffin oil).....	22.50
Methyl violet dye.....	0.75
Nigrosine dye.....	6.
Oleic acid.....	1.50
	126.00

From the above example, it will therefore be seen that a friable resin, glycerol ester of hydrogenated rosin, has been included to aid in hardening of the film thereby contributing to the non-smudging property. The friable resin according to our invention must be compatible with the other components of the ink composition and must be resistant to oxidation and polymerization so that it will retain on long-time aging the properties it exhibits when the ink film first

becomes dry by evaporation of the solvent. In addition to the above identified glycerol ester of hydrogenated rosin other resins of this class include hydrogenated rosin, polymerized resin, chlorinated diphenyls, and arylsulfonamide formaldehyde resins.

The amount of friable resins must be controlled to prevent the film formed on "spot carbonizing" with the transfer ink composition compounded in accordance with this invention from losing its property to transfer.

We have found that by including a film forming material as a reinforcing structure for the non-film forming materials we are able to produce the desired viscosity of the composition for cold solvent application in a printing press or the like and by virtue of its film forming properties the inclusion of such an agent has been found to contribute to the non-smudging characteristic of the dried film. A suitable film forming agent of this kind is ethyl cellulose, or chlorinated rubber, or vinyl resins.

In Example I above the ethyl cellulose N-200 serves in the capacity of a film forming agent. The proportion of the film-forming agent must be kept low in order to retain the transfer properties of the dried ink film.

An important feature of the inclusion of the amide is that not only does it permit with the other constituents the formation of a non-smudging film with highly desirable transfer properties which are retained on long-aging but it has been found to enhance the colour of the ink while not in itself being a coloured compound.

The primary amide of a long-chain fatty acid according to this invention is a primary amide of a fatty acid containing from 6 to 20 carbon atoms in the molecule. Commercially these amides are usually blends of amides of closely related chemical properties. An example of a suitable amide blend consists as described above of 25%, hexadecanamide; 70% octadecanamide; and 5% octadecanamide.

According to this invention the solvent is preferably non-polar to minimize penetration of the paper. The choice of solvent will depend partly on the method of application of the ink to the paper, e. g. doctor blade, the type of paper and composition of the ink. The solvent required must not evaporate too fast yet must afford an ink of a consistency of the order of the grease carbon inks being used at the present time.

We have found that an excellent solvent is an aromatic hydrocarbon having a distillation range between 345° F. and 412° F. This solvent permits of cold solvent application with excellent results with the presence of a filler such as the bentonite clay of the above example.

All solvents having the desired solvent power for dissolving the wax-oil-colour blend, resin, amides, and film former cannot be successfully used as with some their evaporation rate is too high.

By providing a solvent of the type of an aromatic hydrocarbon the solvent power is increased but the evaporation rate is excellent for the cold solvent application. We have found however that it is possible to use these higher power solvents without disturbing the desired consistency of the ink and without in any way destroying the transfer characteristics of the resulting film by incorporating a filler such as the bentonite clay in the ink composition.

Other solvents which permit this invention to

be carried out are chlorinated hydrocarbons, aromatics, paraffins and terpenes.

It will be noted that the inclusion of a filler permits of the use of a solvent affording the necessary characteristics for satisfactory cold solvent application while at the same time maintains in the dried film the desired characteristics of non-smudge and excellent transfer properties initially and on long-time aging. While bentonite clay has been named and bentonite clay of 625 mesh has been found particularly desirable, it will be understood that other clays and for instance whiting can also be successfully employed.

Each of the above ingredients, the wax-oil-colour blend; the filler such as bentonite clay; the friable resin such as glycerol ester of hydrogenated rosin; the primary amide of a long chain fatty acid; and the film former such as ethyl cellulose; carried to the paper in a cold solvent application dissolved or dispersed in a solvent of the nature of an aromatic hydrocarbon, plays an important interrelated role in determining the form of the dried film to provide a cold application film having the characteristics of a non-smudging transfer film which retains its initial transfer properties on aging.

The additives to the wax-oil-colour blend in their proper proportions contribute one or more property to the finished product and several of the additives appear to influence the same property with the result that all the additives unite to form a mixture or blend giving the desired final properties of the cold application ink which have long been sought for in the art.

A further example of a duplicating ink in accordance with this invention is given as Example II below:

Example II

	Parts by weight
Wax-oil-colour blend admixed with bentonite	156
Glycerol ester of hydrogenated rosin	26
A blend of primary amides of long-chain fatty acids	26
Ethyl cellulose N-200	2.6
Aromatic petroleum solvent having a distillation range of 345° F. to 412° F.	172

This above formulation of Example II gives the wax-oil colour blend as admixed with bentonite which mixture may be referred to as a wax-bentonite mixture in accordance with Example II comprises the same mixture as the wax-oil-colour blend and bentonite mixture of Example I above.

To afford a smooth film the bentonite clay is preferably hot milled with the wax-oil-colour blend providing at the same time increased dispersion and grinding of the carbon improving the transfer property of the ink as well as increasing the film smoothness.

The amount of film former such as ethyl cellulose must be retained fairly low to maintain the transfer property of the ink and contrary to what might appear to be the case the film former cannot be relied upon to provide the desired viscosity for printing consistency because of its limitation on the transfer characteristic of the film.

In addition to Examples I and II above other formulae providing the highly desirable non-smudging duplicating ink in accordance with this invention are set forth below, Examples III, IV and V being examples of formulae suitable for use on standard types of printing presses, and Example VI being a formulation suitable for application by means of a doctor blade or scraper blade.

Example III

	Parts by weight
Wax-oil-colour blend	126
Bentonite filler	30
Chlorinated diphenyl resin (softening point: 100° C.-105.5° C.)	26
A blend of primary amides of long-chain fatty acids	26
Ethyl cellulose, N-200	1.3
Aromatic petroleum solvent having a distillation range of 345° F.-412° F.	172

In this example it will be seen that the resin used is chlorinated diphenyl resin.

Example IV

	Parts by weight
Wax-oil-colour blend	126
Bentonite filler	30
Chlorinated diphenyl resin (softening point 100°-105° C.)	26
A blend of primary amides of long-chain fatty acids	26
Chlorinated rubber (125 cps.)	1.3
Aromatic petroleum solvent having a distillation range of 345° F.-412° F.	172

Again it will be seen that the resin used is chlorinated diphenyl resin. The film former used in this formulation is chlorinated rubber.

Example V

	Parts by weight
Wax-oil-colour blend	126
Bentonite filler	30
Aryl sulphonamide-formaldehyde resin	26
A blend of primary amides of long-chain fatty acids	26
Polyvinyl acetate resin (60 cps.)	2.6
Aromatic petroleum solvent having a distillation range of 345° F. to 412° F.	172

This formula shows the use of still a different resin as well as another film forming agent.

It is to be understood that these formulations which are suitable for standard printing press application, are by way of specific examples and not by way of limitation.

Example VI

(Suitable for doctor blade or scraper blade application)

	Parts by weight
Wax-oil-colour blend	126
Bentonite filler	30
Glycerol ester of hydrogenated rosin	78.2
A blend of primary amides of long-chain fatty acids	57.7
Ethylcellulose, N-200	5.2
Aromatic petroleum solvent having a distillation range of 273° F. to 365° F.	660

In this latter example it will be seen that the quantities of resin, amide blend and film forming agent have been increased relative the amount of wax-oil-colour blend and pigment filler, and the amount of solvent has also been materially increased. It will thus be seen that the proportions of ingredients are dependent on the application method, but the novel combination of ingredients is maintained to permit cold solvent application.

In attaining a duplicating ink composition which can be applied to the paper in a cold solvent application and the conception of a cold solvent duplicating ink application wherein no further processing is required after application a definite advance in the manifolding and spot-carbonizing art is presented.

It will be understood that the elimination of the "hot-melt" application and its accompanying disadvantages and the elimination of cold application requiring further film forming processing, much time, labour and money that has previously been expended is eliminated providing a vital reduction in manufacturing costs.

Further, by providing a duplicating ink that can be handled similarly in a printing press to present printing inks, the film can be applied with the same ease and facility and with the same skill as the printing material by the ordinary printer.

Even in addition to facility of application, the present invention affords in the applied film more permanent transfer qualities, better resistance to abrasion, a smoother, more uniform, and better transferring film than has heretofore been provided by other methods.

It will be understood that various changes may be made from the specific examples set forth and various substitutes employed within the scope of this invention where the ink is carried to the paper in a cold solvent application.

In the foregoing, cold solvent application is intended to cover and include those applications wherein the duplicating ink is carried to the paper at temperatures at which ordinary printing ink can be transferred and below that range of temperatures required for the hot-melt process wherein special heating apparatus is required.

What we claim as our invention is:

1. A non-smudging carbon ink for duplicating paper for solvent application comprising, the following ingredients substantially in the proportion set forth by weight, 126 parts wax-oil-colour blend, 30 parts bentonite filler, 26 parts glycerol ester of hydrogenated rosin, 26 parts of a blend of primary amides of long-chain fatty acids, 2.6

parts ethyl cellulose N-200, and 172 parts aromatic petroleum solvent having a distillation range of 345° F. to 412° F. in which the above constituents are dissolved.

2. An ink as claimed in claim 1 in which the blend of primary amides consists of 25 per cent hexadecanamide, 70 per cent octadecanamide, and 5 per cent octadecenamide.

3. A non-smudging duplicating ink for cold application comprising the following ingredients in approximately the following proportions by weight: 126 parts of a wax-oil-colour blend, 30 parts clay filler, 26 parts of a compatible friable resin resistant to oxidation and polymerization, 26 parts of a blend of primary amides of long-chain fatty acids, 1 to 3 parts ethyl cellulose and 172 parts solvent.

WILLIAM N. B. ARMSTRONG.
HYMAN S. KREDENTISER.

References Cited in the file of this patent UNITED STATES PATENTS

Number	Name	Date
1,826,696	Charch	Oct. 6, 1931
2,082,592	Nollau	June 1, 1937
2,147,180	Ubben	Feb. 14, 1939
2,206,636	Hunter	July 2, 1940
2,213,644	Antrim	Sept. 3, 1940
2,275,101	Ellis	Mar. 3, 1942
2,236,812	Wiggam	Aug. 17, 1943

FOREIGN PATENTS

Number	Country	Date
267,625	Great Britain	Mar. 22, 1927
420,545	Great Britain	Nov. 28, 1934
448,578	Great Britain	June 11, 1936
459,344	Great Britain	Jan. 6, 1937
90,199	Sweden	Sept. 14, 1937