Feb. 18, 1969 L. E. THIELEN 3,427,967

METHOD OF PRINTING WITH LOW CONDENSATE PRINTING INK

Original Filed April 25, 1966 Sheet 1 of 2

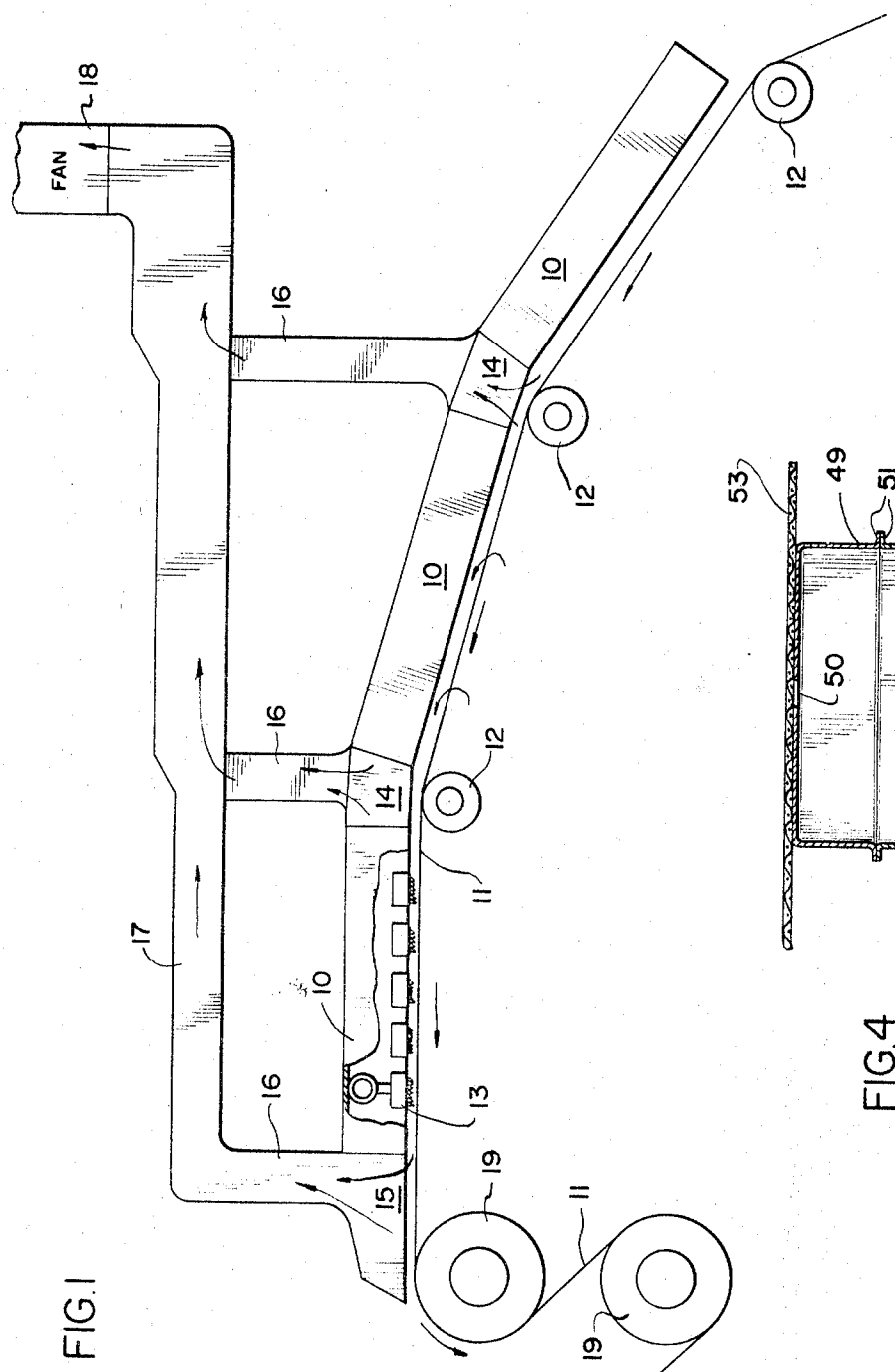


FIG. 1

FIG. 4

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FIG.2

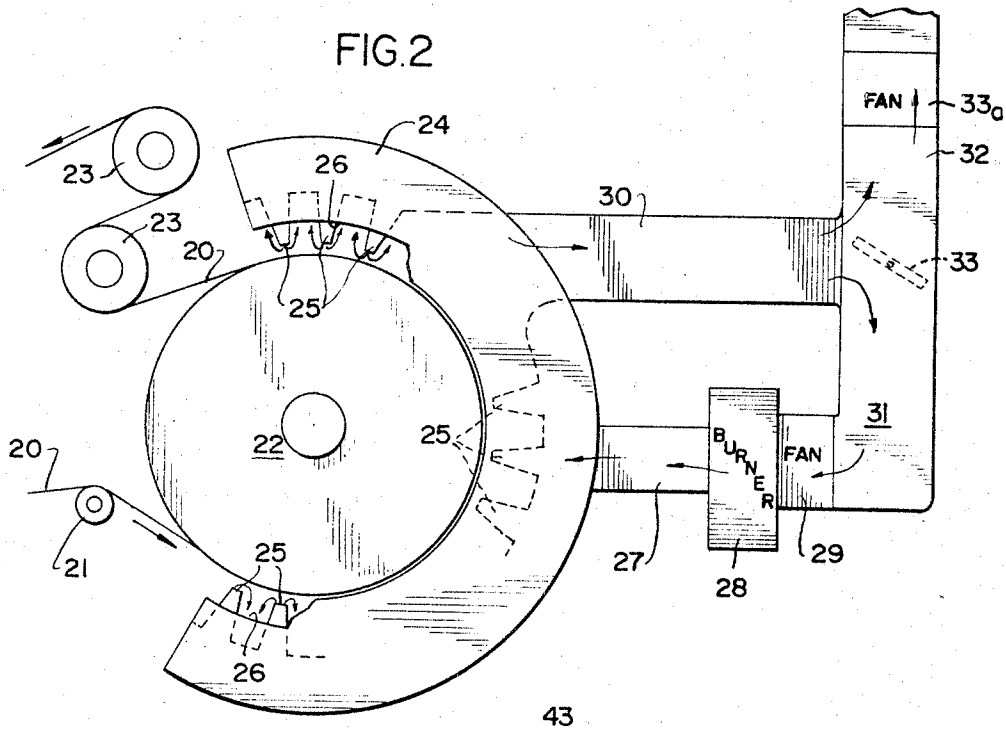
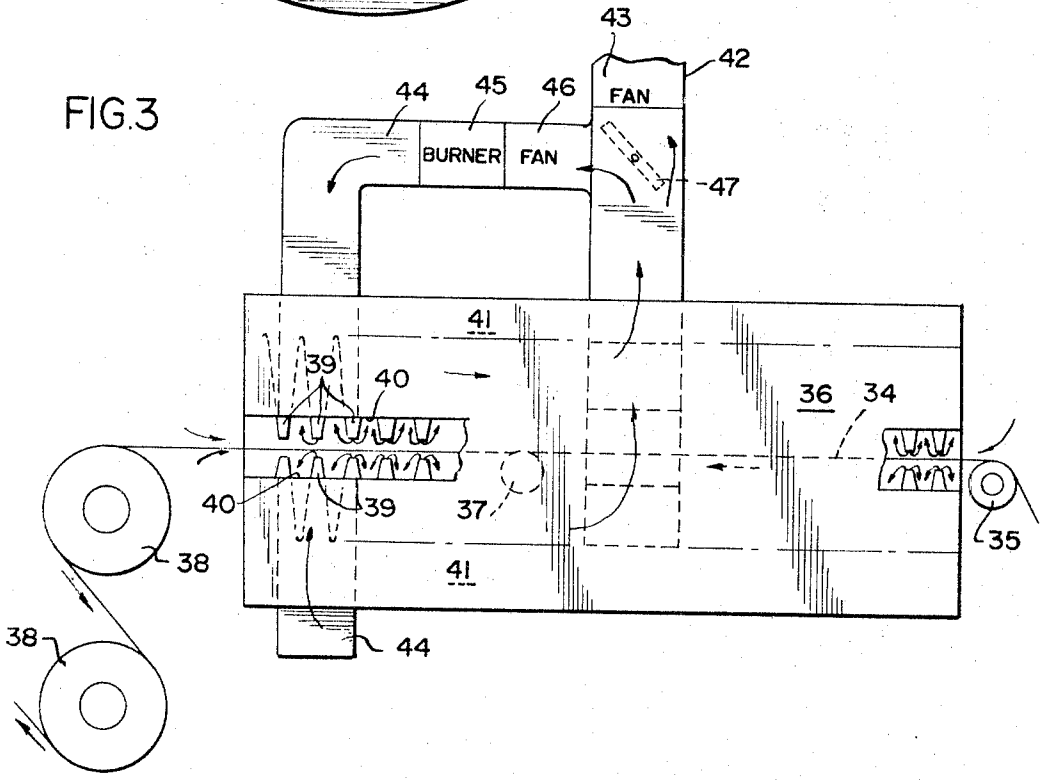


FIG.3



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METHOD OF PRINTING WITH LOW CONDENSATE PRINTING INK

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Continuation of application Ser. No. 544,965, Apr. 25, 1966. This application Nov. 13, 1967, Ser. No. 685,237

U.S. Cl. 101—211 2 Claims

Int. Cl. B41m 1/14

ABSTRACT OF THE DISCLOSURE

A printing ink comprising a hydrocarbon soluble film forming resinous binder together with the solvent, pigment material and additives in which a least 98% of the ink is made up of ingredients that yield less than 6% condensate when measured by The Test Procedure described in the specification hereof with the result that the inks of this invention do not produce condensate streaks in letterpress and offset printing.

This is a continuation of my application Ser. No. 544,965, filed Apr. 25, 1966, now abandoned.

This invention relates to letterpress and offset heat set printing inks and to high speed rotary web fed letterpress and offset printing methods.

The formation of "condensate streaks" on printed paper has been a problem ever since heat set inks were first developed. In spite of many attempts to cure or alleviate this problem, it has up to now not been satisfactorily solved. The nature of the problem in question is explained as follows.

In heat set printing (both letterpress and offset) an ink is used which includes a pigment, a film forming hydrocarbon soluble resinous binder or drying oil, various additives and a hydrocarbon solvent. After the ink has been applied to the paper web the latter is passed through a dryer where the solvent is driven from the ink by the application of heat to the web.

The "condensate streaks" herein referred to may be discolored streaks on printed signatures which are made up of more or less oily, greasy, or tallowy or waxy material which has apparently been volatilized in the course of the drying process and has thereafter been condensed at relatively cool locations where sufficient material can accumulate to form, upon transfer to the printed web, the "condensate streaks" in question. The condensate streaks may also take the form of streaks of resoftened and retransferred ink formed when drops of condensed ink solvent are transferred to the printed paper web where they soften the dried ink and cause its transfer to the opposed paper surface when the paper web is subsequently cut and folded. To explain more fully the formation of condensate streaks, it is necessary to describe in some detail the drying systems conventionally used in association with high speed web fed rotary letterpress and offset printing presses. Such a description is given hereinbelow.

One of the features of this invention therefore is to provide an improved printing ink which avoids condensate streaks in letterpress and offset printing.

Another feature of the invention is to provide an improved method of continuously printing on a moving paper web with a heat setting ink including the step of passing the freshly printed web through a heat setting zone having relatively cool areas without causing condensate streaking on the web.

Other features and advantages of the invention will be apparent from the following description of certain embodiments thereof with the method of the invention being illustrated in several embodiments in the accompanying drawings which also illustrate an apparatus for measuring the condensate of the ink ingredients. Of the drawings:

FIGURE 1 is a fragmentary side elevational diagrammatic view illustrating one apparatus for conventional dryers for heat set printing.

FIGURE 2 is a view similar to FIGURE 1 but illustrating a second conventional dryer.

FIGURE 3 is a view similar to FIGURES 1 and 2 but showing a third embodiment of a conventional dryer.

FIGURE 4 is a diagrammatic vertical symmetrical sectional view through an apparatus for measuring the condensate content of an ink ingredient.

The radiant cup dryer of FIGURE 1 includes a series of three open-bottomed, open-ended boxes **10** arranged in spaced, tandem relationship above the path of the printed web **11** moving in the direction indicated by the arrows from a first set of printing-impression cylinders (not shown), the web being supported while in said path by small internally water cooled idler rolls **12**. Each box has supported therein an array of gas fired radiant ceramic burners **13** facing the web **11**. The boxes **10** are interconnected by hoods **14** and the last box has connected to its exit end an exit hood **15**. Each of these hoods has connected thereto a branch **16** of a main exhaust duct **17** provided with an exhaust fan and a catalytic smoke burner (not shown). From the last of the support rolls **12** the web **11** passes over a pair of large driven internally water cooled chill rolls **19** to a second set of printing-impression cylinders (not shown) followed by a dryer essentially similar to that shown in FIGURE 1.

In the dryer of FIGURE 1, the temperature of the ceramic cups **13** in the radiant burners ranges from 900° F. to 1400° F. (within a single cup), and the web **11** exit temperature ranges from 450° F. to 550° F. The web speed may range from 1500 to 2000 f.p.m.

In the steam drum dryer of FIGURE 2, the printed web **20** passes from a first set of printing-impression cylinders (not shown) over a small infeed idler roll **21**, around a large (6' to 9' diameter) steam drum **22** and thereafter over two large driven internally water cooled chill rolls **23** before being passed over a second set of printing-impression rollers (not shown) and through a second dryer similar to that shown in FIGURE 2. Outside the circumference of the steam drum **22**, and covering the web **20** between the rollers **21** and **23**, there is provided an arcuate hood **24** covering a set of spaced nozzles **25** for directing jets of hot air against the web **20** and, alternating with said jets, exhaust or vent inlets **26** for exhausting the hot air.

The hot air is supplied to the nozzles through a duct **27**, the air being heated by means of a burner **28** and impelled by means of a fan **29**. The exhausted air is withdrawn from the inlets **26** through a duct **30** having a first branch **31** leading to the burner **28** for recirculating a part of the hot air and a second branch **32** having a fan **33** for venting another part of the hot air. A damper **33** at the throat formed where the two ducts **31** and **32** join may be adjusted to vary the ratio of recirculated to vented hot air.

In the dryer of FIGURE 2, the surface temperature of the steam drum **22** is about 340° F.; the hot air is supplied at 350° F. to 700° F.; the web exit temperature is upwards of 350° F. The air exit velocity at the nozzles **25** may be either 4000 to 8000 f.p.m. (specifically, 5000–6000 f.p.m.) or 10,000 to 17,000 f.p.m. In the case of

the lower air velocity, the nozzles are of round cross sectional form; in the case of the 10,000 to 17,000 f.p.m. air velocity the nozzles take the form of slots. The web **20** speed may be 1000 to 1500 f.p.m. when the hot air is supplied at low velocity, or 1500 to 2000 f.p.m. when the air is supplied at high velocity.

In the high velocity hot air dryer of FIGURE 3 the printed paper web **34** passes from a first set of printing-impression cylinders (not shown) first over a small internally water cooled support idler roller **35**, through a dryer hood indicated at **36** optionally including additional water cooled idler support rollers **37** and thereafter over large internally water cooled chill rolls **38**. Thereafter the web passes to a second set of printing-impression rollers (not shown) and through a second dryer essentially identical with that of FIGURE 3. Within the hood **36** there are provided spaced upper and lower air nozzles **39** which direct jets of hot air against both surfaces of the web **34**. This air is vented through exhausts **40** provided between the nozzles **39**. The air from these exhausts moves through ducts **41**, a part being vented through a duct **42** having an exhaust fan **43** and another part being recirculated through a duct **44** leading to the nozzles **39** and having a burner **45** for heating the air and a fan **46**. A damper **47** may be adjusted for varying the ratio of recirculated air to vented air.

In the dryer of FIGURE 3, the air temperature ranges from 350° F. to 600° F. and the web **34** exit temperature ranges upwardly from 300° F. The air velocity at the nozzles is 10,000 to 15,000 or 17,000 f.p.m. The web speed may range from 1500 to 2000 f.p.m.

In the description of FIGURES 1 through 3, reference has been made to printing one side of the webs immediately ahead of the dryers by means of single sets of printing-impression cylinders followed by printing on the other side and drying of the then deposited ink. Such printing, of course, is black on white letterpress printing, and the above reference has been made solely to simplify the description of the dryers. The latter are also used, as is well known, to dry webs subjected to simultaneous printing on both sides by offset methods and to multicolor letterpress or offset printing in which inks of several colors have been deposited on the paper web in rapid succession and without drying the ink before the next impression is made. Such multicolor printing may involve a single impression cylinder and several printing cylinders associated therewith, or it may be done by means of successive sets of printing-impression cylinders. Since ordinarily more ink is deposited on the paper in four color printing, it is obvious that four color printing is likely to be more troublesome, from the standpoint of "condensate streaking" than black on white printing, and therefore the present invention is of particular utility when applied to four color printing.

It will be noted that in the dryers of FIGURES 1 through 3 there are a number of areas where volatilized ink material may condense and collect. Examples are the chill rolls **19**, **23** and **38**, the support rolls **12** and **37**, the hoods **14** and **15**, and the exhaust ducts **14**, **15**, **16**, **17**, **30**, **41** and **42**. In all these areas, surfaces that are contacted by volatilized material are kept at a relatively low temperature, either by water cooling, as in the case of the rolls, or by contact with the atmosphere, as in the case of the hoods and the exhaust ducts. Further, condensate can collect or accumulate at these locations. The paper web is separated, at high web speeds, from the chill rolls **19**, **23**, **34** and **38**, and from the support rolls **12** and **37**, by a cushion or layer of air, and streaking of the web does not occur until sufficient condensed material has accumulated on the roll to bridge the air gap and to streak or spot the web unless, as sometimes happens, the web from time to time bounces into contact with the roll.

In the hoods **14** and **15**, and in the exhaust ducts **17**, **27**, **30**, **31**, **32**, **41** and **44**, material can condense and collect until the aggregate mass grows to the point where it will no longer adhere to the wall surface but will drip off and flow or fall onto the paper web. It may be noted that the condensate formed on the water cooled rollers is sometimes solid at room temperature yet generally includes more volatile and less easily condensible material than the condensate formed on the hood and duct walls. The condensate on the support rollers may even be largely ink solvent. The condensate formed on the hood and duct walls tends to include high boiling material of higher melting point which, when condensed, is pasty or solid rather than fluid. Further, this latter condensate is often quite tacky and is therefore apt, when falling onto the paper web, to cause web breaks. It is sometimes referred to as "rosin drip."

The tendency to generation of condensate streaks depends, among other things, (1) on the composition of the printing inks and (2) on the conditions prevailing in the printing press and in the dryer associated therewith. The present invention relates to an ink composition which reduces or eliminates condensate streaks, as explained hereinbelow. However, the second factor (printing press and dryer conditions) requires some discussion in order to illustrate the gains made possible by the reduction or elimination of condensate streaks.

Assuming a sufficient heat transfer to the web to effect at least reasonably complete drying, high web speed and heavily inked forms or printing plates tend to cause generation of condensate streaks. Under such operating conditions, large volumes of vapors are generated in the dryer, and these vapors are not removed fast enough from the dryer so that some condensation will take place. A generally accepted expedient for drying when condensate streaks are encountered is to reduce press speed to the point where condensate streaks are largely eliminated. This expedient is not always successful, but it succeeds, if at all, at the cost of severely reducing the productivity of the press. Thus, elimination or reduction of condensate streaks will directly increase the productivity of a heat set rotary printing press.

I have now found that condensate streaks may be greatly reduced or eliminated by printing with inks formulated from conventional ink ingredients according to conventional formulating principles as long as at least 98% of the ink is made up of ingredients which meet the requirement of a test described as follows and utilizing equipment as shown in FIGURE 4.

THE TEST PROCEDURE

The test samples are 1 gram. Each sample is placed in an aluminum foil (0.003" thick) round pan **48** that is 2¼" in diameter and ⅝" high (Fisher cat. No. 8–732–5, size C). The pan is then covered with a similar inverted pan **49** of known weight formed with a central aperture **50** that is 5/16" in diameter. The pans **48** and **49** are each formed with a ⅛" wide outturned flange **51** so that the superposed pans can be held together by paper clips (not shown). The pans are protected from drafts while heated for one hour on a hot plate **52** having a surface temperature of 610° F. to 630° F. More specifically, I use a Schaar Scientific 3600 watt, cat. No. G8330, 18" x 24" surface hot plate with all circuits on, and adjusted by means of a 220 volt heavy duty 30 amp. to control the temperature of heating by selecting an area having a surface temperature of 630° F. to 610° F. I use an Alnor 0° F.–1000° F. Thermocon Type 4200A contact pyrometer having a 4040 tip with a self-contained cold junction calibration spot.

By means of this pyrometer a central constant maximum temperature is located on the hot plate surface and its temperature is adjusted to 630° F. Then the temperature range of the hot plate surface, with the exception of a peripheral 4" wide band (which is not used) will be 630° F. to 610° F. In this zone 15 samples can be run simultaneously. To insure good contact a steel screen **53**

is placed on top of the pans. This screen is coarse enough so that none of the 3/16" openings is even partially blocked. The sample pans are huddled on the central calibrated area without contacting each other. The area of screen contact with the pans is minimal so that the screen does not act as a cooling drain or heat sink.

The hot plate is brought to its desired high temperature and kept there for a few hours before the samples are placed thereon. After an hour of heating the pans are removed and cooled. The inverted collection pans **49** are weighed, and the weight gain for the inverted collection pan is noted and the amount of condensate collected is computed as percent of the original sample.

Preferably, the determination of condensate collected is run in triplicate. If one result varies widely from the other two, the one must be disregarded. According to the standard of the present invention, at least 98% of the ink must be made up of ingredients that yield not more than 6% collected condensate as determined by the above described test procedure.

Specifically, this test is applied to each and every ingredient, and not to mixtures of some ink ingredients, nor to finished inks. There are some finished complete inks that when tested yield less than 6% of collected condensate but still tend to form condensate streaks, although other inks having such low condensate yields do not. But finished complete inks that yield more than 6% collected condensate do tend to form condensate streaks. The same is true of mixtures of ink ingredients such as pigment flushes which ordinarily include pigments, varnishes and surface active components. These flushes, constituting pigment plus vehicle, are normally used in an amount of at least about 2% of the ink. There is no practical reason to use more than about 60%. A pigment flush may yield less than 6% collected condensate although one or more components yield more than 6%. A flush containing such components should not be used in making the inks of this invention regardless of the low collected condensate value obtained when this flush is tested if as a result of such use the finished ink would contain more than 2% of ingredients yielding more than 6% condensate. Neither should a flush be used that when tested yields more than 6% collected condensate.

Conventional ink ingredients that yield more than 6% collected condensate may not be included in inks according to the present invention in a total amount exceeding 2%. Examples of such conventional ink ingredients are wood rosin, gum rosin, dimerized rosins, calcium and zinc rosin salts, rosin esters such as the pentaerythritol ester, coumarone-indene resins, copolymers of methyl styrene and vinyl toluene, linseed oil-phthalic anhydride esterified with pentaerythritol, polyurethane, many linseed oil and linseed oil varnishes, bodied soya oil, dehydrated castor oil, stearic acid, aluminum stearate, lanolin, lecithin, petrolatum, methyl violet toner containing fatty acids, alkali blue toner containing linseed oil, highly resinated toners and lakes, and pigments and lakes flushed in linseed and other varnishes.

Examples of ink ingredients yielding 6% or less collected condensate are given below.

Resins include most high grade Gilsonites; "Inkovar 180" (a Pennsylvania Industrial Chemical Corporation cyclopentadiene type heat polymer having a minimum ball and ring softening point of 177° C., an acid number of less than 1, and soluble in a typical gravure solvent of at least 55% solids at 20° C.); Pentalyn X (a Hercules maleic modified pentaerythritol ester of rosin soluble in aliphatic and aromatic hydrocarbons); Pentalyn 802A and Pentalyn 833 (both Hercules phenolic-modified pentaerythritol rosin esters partly soluble in petroleum hydrocarbons); "Arochem 605" (an Archer-Daniels-Midland pentaerythritol ester of fumaric and maleic ester soluble in aliphatic hydrocarbons); polycarbonates; phenoxy resins; methyl methacrylate resins; polysulfone resins; and polyphenylene oxide resins.

Drying oils that may be used include some polymerized linseed oils, bodied wood oil and bleached safflower oil.

Certain gloss varnishes (which are reaction products and not simple solutions or mixtures of ingredients) may also be used in preparing the inks of the present invention. Many available gloss varnishes, however, yield more than 6% collected condensate. I therefore give below directions for making gloss varnishes that yield 6% or less collected condensate.

The following gloss varnishes are prepared under a blanket of nitrogen or carbon dioxide, preferably in a stainless steel kettle, with smooth, adequate agitation and evenly applied heat.

Gloss varnish No. 1

239 parts polymerized linseed oil, 60 parts pentaerythritol and 0.15 part $Ca(OH)_2$ or PbO catalyst are reacted. Specifically, while the linseed oil is heated at 480° F. one half of the pentaerythritol is added. After 10 minutes, or when a clear liquid has been formed, the remaining pentaerythritol is added. After 40 additional minutes of heating the reaction is reasonably complete. One milliliter of the product should be soluble in 3½ milliliters anhydrous methanol at room temperature. The final acid number should be less than 10.

The above reaction product is further reacted as follows. 39 parts reaction product, 20 parts 80% dimerized rosin, 10.2 parts pentaerythritol, 20.1 parts isophthalic acid, 0.8 part maleic anhydride and 0.9 part fumaric acid are heated together and gradually raised to 560° F. where the mixture is held until an acid number of less than 10 is reached. Usually 4 to 6 hours are required. The resulting gloss varnish must yield less than 6% collected condensate.

Gloss varnish No. 2

130 parts rosin are melted in a kettle. While the molten rosin is being stirred, 4 parts fumaric acid and 2 parts maleic anhydride are added. 0.1 part phosphoric acid is then slowly added. Heating at 400° F. is continued for 2 hours. The temperature is gradually raised to 560° F. while 11 parts pentaerythritol is gradually added. Heating at 560° F. is continued for about 6 hours until the reaction is complete and the acid number is 10 to 15. The product should yield less than 6% collected condensate.

Pigments and extenders that may be used include chrome yellow, phloxine toner, lithol rubine, cyan blue, peacock blue, channel black, furnace black, phthalocyanine blue and green, toluidine red, chrome or milori green, chrome orange, iron blue, clay, aluminum hydrate, blanc fixe, calcium carbonate, magnesium oxide and titanium dioxide.

Solvents that may be used include the usual aliphatic and aromatic hydrocarbon solvents included in heat set printing inks. The usual petroleum fractions are conventionally identified by the boiling point of the first 5% fraction, e.g. 440 oil or 470 oil. Very high boiling petroleum fractions such as are used in formulating news inks (boiling point 650° F. or higher) yield excessive amounts of collected condensate and should not be included with the inks of this invention except as a part of the total 2% of allowable high collected condensate material.

Additives are materials included with printing inks to influence properties such as body, viscosity, gelling, scuff resistance, rub or smear resistance, gloss, toughness and ink trapping. Examples of additives that may be used are aluminum octoate and calcium stearate which yield less than 6% collected condensate. Some additives yielding more than 6% collected condensate may be used in amounts ranging up to 2% of the ink. Thus, polyethylene of about 2,000–500,000 molecular weight may be used in the form of a "wax compound" made up of 15% polyethylene, 42.5% Inkovar 180 or other resin yielding less than 6% collected condensate, and 42.5% solvent such as 470 oil.

Examples of specific ink formulations are given as follows:

Example 1.—Black letterpress ink

	Percent
Furnace black	18.4
Clay	11.7
Alumina hydrate extender	1.1
Gilsonite	24.1
470 oil	44.7
	100.0

Example 2.—Black letterpress or web offset ink

	Percent
Channel black	13.3
Polyethylene wax compound	4.2
Gloss varnish	6.2
Inkovar 180	18.2
Gilsonite	9.2
440 oil	46.8
Toner	2.1
	100.0

Example 3.—Red letterpress ink

	Percent
Phloxine red	15.7
Polyethylene wax compound	4.3
Gloss varnish	6.1
Inkovar 180	30.0
470 oil	43.9
	100.0

Example 4.—Red letterpress or web offset ink

	Percent
Lithol rubine	13.1
Polyethylene wax compound	5.0
Gloss varnish	15.8
Inkovar 180	21.3
500 oil	44.8
	100.0

Example 5.—Yellow letterpress or web offset ink

	Percent
Benzidine yellow	9.9
Chrome yellow	19.8
Inkovar 180	20.8
Gloss varnish	13.1
Polyethylene wax compound	4.0
470 oil	32.4
	100.0

Example 6.—Yellow letterpress or web offset ink

	Percent
Chrome yellow	23.1
Gloss varnish	37.2
Polyethylene wax compound	4.8
470 oil	34.9
	100.0

Example 7.—Blue letterpress or web offset flush or concentrate

	Percent
Phthalocyanine blue	26.1
Phthalocyanine green	2.6
Inkovar 180 varnish (60%/470 oil)	39.1
Gloss varnish (60%/470 oil)	25.2
470 oil	7.0
	100.0

Example 8.—Blue letterpress ink

	Percent
Peacock blue	8.2
Phthalocyanine blue	0.8
Inkovar 180	22.2
Gloss varnish	16.7
Polyethylene wax compound	6.1
470 oil	46.0
	100.0

Example 9.—Blue letterpress or web offset ink

	Percent
Phthalocyanine blue	7.3
Phthalocyanine green	0.8
Inkovar 180	21.3
Gloss varnish	18.4
Polyethylene wax compound	3.5
470 oil	48.7
	100.0

The above inks can be made by any conventional method, as by stirring the ingredients together and then passing the resulting mixture through an ink mill. Or the gloss varnish and/or resin dissolved in solvent can be used to flush the pigment to form a concentrate (as in Example 7) which is then diluted with solvent to make the finished ink.

It should be noted that for the purpose of the present invention each one of the inks used in multicolor printing must meet the requirements herein stated, and that the same applies to the inks used on the opposite sides of a paper web, since otherwise condensate streaking will take place. Obviously, any one ink laid down on a paper web can cause condensate streaking on this web, regardless of what other inks may also be laid down on this web. Further, condensate streaking may be due to the cumulative effect of several inks deposited on a paper web, even though conceivably each ink, laid down by itself, would not cause condensate streaking. Some conventional inks cause condensate streaking under all except the most favorable conditions. Other conventional inks do not cause condensate streaking except under adverse conditions such as high web speed, excessive general or local dryer temperatures, heavy forms, low cooling water temperature, low ambient temperature and/or the presence of other inks tending to form condensate streaks. The inks of the present invention, on the other hand, do not form condensate streaks even under the above noted adverse conditions, or in any case can tolerate much more adverse conditions than conventional inks.

The inks of the present invention are generally characterized by good release of relatively low boiling solvents such as 440, 470 and 500 oil, which are the preferred solvents. Therefore, the solvent content of the ink is released quickly and early in the drying process, so that the resulting vapors are evacuated rapidly from the dryer and are not carried along to the cool and chilled roller surfaces where they would be condensed. Thus the present invention serves to reduce or eliminate the wetting of the paper web with condensed solvent which would resoften the dried ink.

All amounts, parts and percentages herein are by weight.

Having described my invention as related to the embodiments set out herein, it is my intention that the invention be not limited by any of the details of description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

I claim:

1. In a method of continuously printing on a moving paper web with a heat setting ink including the step of passing the freshly printed web through a heat setting

zone having relatively cool areas, the improvement comprising: printing on said web without producing substantial condensate streaking with a substantially condensate free ink comprising a hydrocarbon soluble film forming resinous binder, a hydrocarbon solvent therefor, pigment material, and additives for controlling the printing properties of said ink, at least 98% of said ink being made up of ingredients each yielding less than 6% condensate when measured by the method of The Test Procedure described in the specification hereof; and heating said printed web to heat set the ink.

2. The method of claim 1 wherein said web is printed with a successive series of inks prior to said heating to heat set all said inks.

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WILLIAM B. PENN, *Primary Examiner.*

U.S. Cl. X.R.

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