https://doi.org/10.2352/ISSN.2169-4451.2018.34.44

Tall Oil Rosin: A Substitute for Gum Rosin in Development of Offset Printing Ink

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Abstract

Gum rosin based resin is widely used in manufacturing of offset printing inks, because of its robust chemical and physical properties. However, another by-product obtained in the kraft pulping process, by distillation of crude tall oil is tall oil rosin. The rosin acid content in the tall oil rosin makes the resin made from it especially of interest to the ink maker. Moreover, tall oil resin offers some economic benefit over gum resin. This work involves exploring the viability of using inks made from tall oil rosin based resin and whether it can be used as a suitable substitute for gum rosin based resin, especially for being used in package printing purposes, which requires ink having good gloss and quick-drying properties at the same time. In this work a varnish was made from tall oil resin and was characterized. Finally complete process set of finished inks were made from both tall oil resin and gum resin and their properties were compared.

Introduction

The printing industry today is driven primarily by the growth in packaging applications. The global printing market value is set to reach $814.5 billion in 2022 [1].The primary components of printing inks used for traditional lithographic processes include, a varnish, colorant and a few additives. The varnish is at the heart of any printing ink, it helps not only to disperse the colorant, but binds the ink to the substrate. The rheology of the inks used for lithographic process are specific, where the inks are characterized by high viscosity and tack. The varnish used for manufacturing such inks hence are highly viscous in nature, which are prepared by cooking the resin in an oil medium over a period of time [2-7]. Traditionally resins commonly used for these purposes contain compounds which might cause VOC emissions [8-9]. However, with the advent of regulatory compliances, manufacturers are moving towards using materials from renewable sources and creating products which are bio-degradable. A major source of resin is rosin, whose predominant component is abietic acid. Rosin contains some high molecular weight diterpenic monocarboxylic acids, which are known as resin acids [10-11]. Apart from which, they also contain some esters, alcohols and other hydrocarbons. Rosin based resin synthesis involves isomerization of rosin to obtain levopimaric acid [12]. Following which, diels-alder reaction occurs between the former and maleic anhydride to form rosin-maleic adduct. The next step involves a resol formation in the presence of an alkyl phenol and para substituted formaldehyde. Finally in presence of a polyol, the resol adduct undergoes an esterification process to form the modified rosin based resin [13].

Most of the rosin used in the synthesis of resin is sourced from gum rosin. It is obtained as the residue from the distillation of turpentine from crude turpentine pitch [14]. In this work however, an investigation has been conducted on whether, the gum-rosin can be substituted with tall oil rosin, which is obtained from pine trees and also as a by-product of kraft pulping process. The primary components of pine wood include cellulose, hemicellulose, lignin, turpentine and tall oil. In the sulphate pulping process, the chips are digested to isolate the cellulose and hemicellulose from the remaining components which are obtained as a “black-liquor” [15-16]. This liquor is then evaporated and acidified using sulphuric acid to produce crude tall oil (CTO). The CTO is then fractionated to obtain components like tall oil heads, tall oil fatty acids, distilled tall oil fatty acids, tall oil rosin, tall oil pitch [17]. Tall oil rosin contain greater percentage of abietic acid than gum rosin, and most importantly, the quantity of pimarane-type acids is less compared to abietic type. Consequently, increasing the possibility of chemical reactivity of tall oil rosins. Apart from this, specific gravity, saponification value, and melting point of tall oil rosins are similar to that of gum rosin [18], making it a suitable contender for being used in the manufacturing of printing inks and coatings. The acid value of tall oil rosin is higher than that of gum rosin, increasing their gelling characteristics in varnishes due to increased solution viscosity. Moreover, tall oil rosin being a by-product of the kraft process, it has a distinct advantage of being cheaper compared to other rosin sources, which makes it useful in large scale ink manufacturing process. CTO forms about 3% of the total weight of pine wood and contributes to $10 billion to the pine chemical industry [19]. Although the availability of CTO is linked to fuel prices and supply chain, however, the global market for tall oil is expected to rise substantially [20].The supply of tall oil has risen to 1.6 million metric tons per year globally in 2006. All these factors can help tall oil rosins become a stable source of resin production in the ink industry.

In this work, an investigation was conducted to verify whether tall oil rosin based resin can be used as a stable source of resin for the synthesis of oleo-resinous printing inks for lithographic applications, especially those used for package printing.

Experimental Procedure

Printing inks have been synthesized using tall oil rosin based resin, instead of gum rosin, keeping all other ingredients unaltered. This has two-fold purpose, to verify whether tall oil rosin based resin is compatible with varnish system presently used and secondly, to analyze whether the ink prepared from tall oil resin is suitable to be used as a substitute for gum resin based inks for application in offset based package printing. The first step in the work involved synthesis of varnish from the standard gum rosin based resin and tall oil rosin based resin, followed by testing and characterizing the said varnishes. Once the varnishes had been prepared and characterized, final printing inks were made and their properties were tested and compared.

Varnish preparation involved charging the vegetable oil into a flask and heating it in an inert medium. Alkali refined linseed oil was used for preparing the varnish, because alkali refining eliminates gums and phospholipids that might alter properties of the ink. This also reduces free fatty acid content, thereby reducing hydrophobicity [21]. Heating the oil accelerates its polymerization, while the inert medium prevents the darkening of the oil. Once the sufficient temperature was reached, the tall-oil based resin was added and the temperature was further increased for "cooking" the resin in oil. The next step involved adding low aromatic content distillate. This stage in varnish preparation is known as a "pregel" stage. The varnish made at this point was tested for its properties and was characterized. In a further stage, aluminum based chelate was added as a gelant to the "pregel" to increase viscosity of the varnish.

Table 1: Results of varnish testing

Properties	Gum resin based varnish	Tall oil resin based varnish
Pre-gel		
Viscosity (30^0C, Poise)	360	360
Yield Value (dyne/cm^2)	6000	10000
Tack (G-m, 800 rpm, 90^0F)	10	11
Heptane tolerance (c.c.)	9	10.1
Final		
Viscosity (30^0C, Poise)	600	600
Yield Value (dyne/cm^2)	15000	14000
Tack (G-m, 800 rpm, 90^0F)	11.3	12.8
Heptane tolerance (c.c.)	9.8	11
Emulsification		
Initial torque	627	658
Differential torque	296	204
Emulsification capacity	60 – 70	40 – 50

Gelling the varnish presents some distinct advantages to the ink-maker. It has an immediate effect in increasing the viscosity of the varnish. This helps in preventing excess absorption of the ink into the substrate after printing, thereby maintaining gloss. Furthermore, since the gelled varnishes offer higher solution viscosity, using such varnishes also reduces the chances of problems like ink misting [22]. This varnish was characterized and was further used to prepare finished ink.

The final process set of inks were made in three phases, which included, mixing the pigment within the varnish in a saw tooth mixer, followed by dispersing the mixture in a triple roll grinding mill and finally adding additives to the dispersed ink. The properties of the said finished inks were then tested.

Results and Analysis

For the purpose of testing the solubility of the resin, it was diluted in toluene at 35% and 50% concentrations. The viscosity of tall oil resin in toluene solution was comparable to the standard gum resin, while the heptane tolerance was higher, suggesting that solubility of tall oil resin was higher in the same solvent medium, and that the resin is compatible with the varnish used for preparation of the inks. Increased solubility of the resin is also likely to improve optical properties of the finished ink.

Table 1 provides all the data pertaining to the results obtained from varnish testing. The physical properties of both the "pre-gelled" and "gelled" varnishes made from gum- rosin-based resin and tall-oil-rosin-based resin were examined. For the pre-gelled varnish, it was observed that while viscosity for both the varnishes were comparable, the yield value of the tall-oil resin based varnish was higher than the standard gum resin based varnish. A higher yield value is likely to improve the runnability of the finished ink, as the ink will have better tolerance towards shearing forces acting upon it in an offset machine. As for the final gelled varnish, the viscosity and yield value of both the varnishes increased, however the yield value of both the varnishes was comparable. Tack and heptane tolerance for tall oil resin based varnish was higher than the standard varnish in both pre-gel and final stages of varnish synthesis. As observed earlier, increased solubility of the resin is likely to give the finished ink better optical properties, while the higher tack suggests increased cohesive forces with the varnish. Tack is the property which ensures steady transfer of the ink from the ink fountain to the substrate via the inking system. The tack values obtained for the tall oil resin based varnish is higher than the standard varnish, although it is within tolerance levels which makes it suitable for making offset printing inks. Another important parameter that is essential to consider is the capability of the ink to form a water-in-ink emulsion during lithographic printing. The lithographic property of the varnish has a significant impact on the emulsification capability of the finished ink, hence the emulsification properties of the final

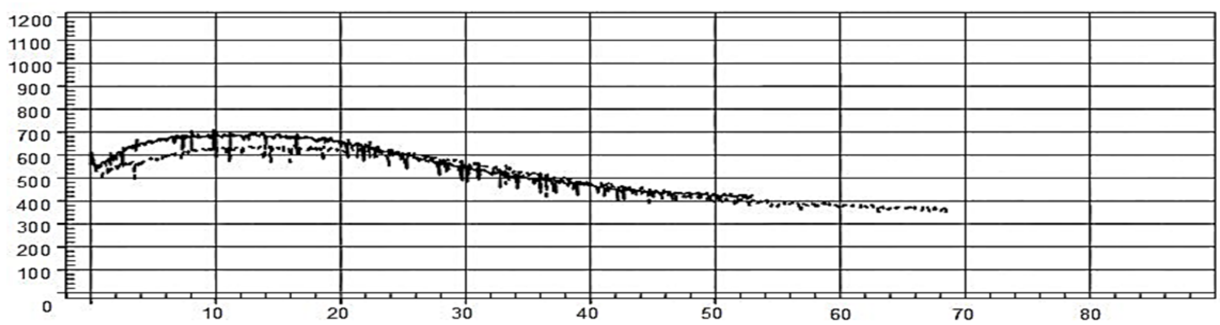

***Figure 1:** Emulsification curve for varnish prepared with tall oil resin (continuous line) and gum resin (broken line)*

Table 2: Comparative data obtained from inks prepared from gum resin based varnish (Std) and tall oil resin based varnish (Exp)

	Yellow		Magenta		Cyan		Black	
Properties	Std	Exp	Std	Exp	Std	Exp	Std	Exp
Dispersion (µm)	13	13	13	13	13	13	13	13
Viscosity (Poise)	160	180	240	240	220	230	220	210
Yield value (dyne/cm^2)	4000	8000	4000	10000	5000	4000	5000	4000
Tack (G-m, 800 rpm, 90^{0}F)	10.7	11	11.2	11	11.5	11.7	12.5	12.7
Flow (cm, 30^{0}C, 10min, 90^0)	14	14	15	15	14	13	14	15
Print properties (gloss art 130 gsm paper) at same volume(0.125 cc)								
Optical density	1.87	1.82	2.32	2.23	2.37	2.34	2.62	2.62
Gloss (60^0)	65	68	54	58	46	48	61	63
Print properties (gloss art 130 gsm paper) at same transfer (1.43)								
Optical density	1.88	1.88	2.28	2.3	2.37	2.34	2.62	2.62
Gloss (60^0)	63	68	52	57	46	48	61	63
Setting (min)	3.0 – 3.5	3.0 – 3.5	3.0 – 3.5	3.0 – 3.5	2.5 – 3.0	2.5 – 3.0	3.0 – 3.5	3.5 – 4.0
Rub resistance								
After 90 min	70	70	70	70	70	70	60	70
After 24 hours	70	70	70	70	70	70	70	75
Substrate drying (min)	740	660	175	150	265	285	310	330
Blocking	65	75	65	70	70	65	50	50
Opening time (hours)	28	22	26	25	25	26	26	27
Skinning time (days)	>3 days	>3 days	>3days	>3 days	>3 days	>3 days	>3 days	>3 days
Emulsification								
Initial torque	557	552	576	660	576	580	576	580
Differential torque	130	120	74	104	105	100	105	100
Emulsification capacity	70 – 80	60 – 70	80 – 90	65 – 75	80 – 90	70 – 80	80 – 90	70 – 80

gelled varnish was also tested using a lithotronic emulsification tester. Figure 1 provides the emulsification plot of both the varnishes, where, the emulsion behavior of tall oil resin based varnish has been plotted with continuous line and that for the gum resin based varnish using broken line. It should be noted that the overall nature of the curve plotted for the tall oil resin based varnish (as well as the existing varnish) had no abrupt fall in torque values, meaning that the varnish has the ability to form a stable emulsion without losing its rheological integrity, making it a suitable contender for being used in the manufacturing of offset printing inks. It was observed that the initial torque for the tall oil resin based varnish was higher. Higher initial torque might lead to better shear resistance of the ink. The differential torque value for tall oil resin based varnish was lower, suggesting that ink made with such a varnish would produce stable water-in-ink emulsion during press operations. However, the total water uptake for tall oil resin based varnish was lower compared to gum resin based varnish, meaning that the maximum amount of water that the ink could accept before forming an ink-in-water emulsion is lower for tall oil resin based varnish. Further examination of the emulsification capability of the final inks made with both the varnishes have been stated later in this section.

Owing to higher heptane tolerance of the tall oil resin in solvent, it was expected that the ink prepared from such resin was likely to have good pigment dispersion and gloss properties. This was verified by testing the properties of the finished inks prepared from the gum resin and tall oil resin based varnishes. It was observed that the tall oil resin ink attained superior pigment dispersion within a single dispersion stage.

Entire process set of offset ink, comprising yellow, magenta, cyan and black were made from both gum-resin based varnish and tall oil resin based varnish. Results from the tests conducted on the process inks made from gum resin against tall oil resin has been summarized in Table 2. Viscosity, tack and flow were comparable for all inks. Yield value was higher for yellow and magenta tall oil resin based inks, which shall prove to be advantageous during press operations and prevent adverse effect on the ink due to shearing forces on the ink during metering through the inking system. The yield value for cyan and black inks made from tall oil resin and gum resin were comparable. In order to test the optical properties of the inks, two sets of laboratory prints were drawn using printability tester, one with equal volume and the other with equal transfer. Considering a standard volume of two different inks that is being used for printing on the same type of substrates for comparative analysis, the results obtained from such prints may vary widely. The reason for this is the fact that ink-substrate interactions are dependent on the rheology of the ink and the capability of the substrate to absorb the ink [23]. For the same ink, the nature of print may vary if the substrate is varied. Conversely, for the same substrate, the nature of prints may vary if different inks are being chosen having different rheological properties. The actual optical properties of the ink may not be accurately inferred from the results arising out of prints taken with same volume of ink. Hence, it is not sufficient to draw prints using equivalent volumes of ink, but what is essential is to draw prints on substrates such that actual transfer of ink is same, thereby making the nature of print independent and exclusive to the external factors arising out due to ink-substrate interactions. For prints drawn with same volume, the results suggested that the optical density of both set of inks were similar. Gloss measured at 60 degree geometry was higher for tall oil resin based ink compared to gum resin based inks. For prints drawn at same transfer rates, the optical density for both set of inks were similar. And the gloss for tall oil resin based inks was higher than their gum resin based counterparts. It was also observed that setting times for both inks of all colors were comparable. The important aspect to consider is the fact, that owing to higher resin solubility, the gloss for tall oil resin based inks were higher than gum resin based inks, but not at the cost of their drying properties. The tall oil resin based inks offer high gloss along with quick setting times, which clearly proves to be an edge over conventional gum resin based inks. To further investigate the drying capability of the ink, substrate drying times were tested. The results suggested that substrate drying times for tall oil resin based ink was substantially quicker than the standard ink for yellow and magenta colors, making them ideal for being used as "quick-set" inks. While the substrate drying time for cyan and black tall oil resin based inks was marginally higher than those for gum resin based inks. Time for a 37 µm thick ink film to dry on a non-absorbent surface was tested to check for the ink opening time, the results showed that time for the ink film to dry was low for yellow tall oil resin based ink and that for other colors were comparable with gum resin based ink. This test suggests the surface film drying capability of the inks, lower values are better. Skinning time refers to the time by which the top surface of a bulk ink will undergo oxidative-polymerization when left unaffected, and eventually form a hard layer along the top surface of the ink. Usually, this time is essential in the press because formation of an oxidized layer on the ink placed in the ink fountain during press operation is unwanted, as it will lead to a variety of print problems. Generally, skinning times are expected to be upwards of 2 days. And it was observed from the results that for both set of inks of all colors, skinning times were higher than 3 days.

Post print characteristics were also tested. With high speed modern sheet-fed offset machines, it is essential that ink dries as quickly as possible. This is of primary importance, because freshly printed sheets getting stacked on top of yet uncured sheet might lead to what is known as "set-off" problem, in which the uncured ink from the sheet might get transferred onto the rear of the succeeding sheet, thereby leading to loss of ink from the preceding sheet. To ensure that the ink has very quick surface curing properties, so that "set-off" doesn't occur under stack pressure at delivery end of the sheet-fed offset machine, a blocking test is performed. In this test, pair of prints were drawn using two inks of the same color, where one ink was tall oil resin based and the other was gum resin based and they were kept open for two minutes. Following which, an unprinted sheet of the same nature on which the prints were drawn, was placed on top of the prints along with a small stack of other sheets of the same size as the prints, and finally a weight of 10 kg was placed on top of it all, to simulate the pressure exerted by the printed stack in the offset press. It was kept for 24 hours and the unprinted sheets were separated and were observed. The results are a comparative analysis between pairs of ink of different colors, where higher scores indicate better ink retention on the printed substrate without leading to "set-off". It was observed that yellow and magenta of tall oil resin based inks had better block resistance, while cyan had poorer and black had similar block resistance in comparison to gum resin based inks.

Rub resistance is performed by drawing prints of pair of inks under same conditions and then mechanically rubbing two sets of the surface of the print against an unprinted surface of the same substrate, one after 90 minutes from drawing the print and the other after 24 hours. This test is a metric which determines how well the surface of a dried ink film on substrate is resistant to abrasion. The more ink is transferred to the unprinted substrate from the print, the poorer is the abrasion resistance of the ink. Results show that both the inks had comparable rub resistance for yellow, magenta and cyan. But the rub resistance of black ink made from tall oil resin was higher than that made from gum resin.

The emulsification properties of the inks were found to be in line with that of the varnish. Emulsification study was conducted and it was observed that the yellow, cyan and magenta tall oil resin based ink had lower differential torque values than the standard ink, which suggests that the former was likely to form more stable emulsion with water during actual press operation. However, the same is higher in magenta tall oil based ink. The amount of water that the ink takes up while printing operation defines various aspects of the print quality. The expected outcome from water and ink interactions in offset printing is the formation of water-in-ink emulsion. If the ink accepts higher amounts of water, then naturally, the ink film drying times on substrate will be higher, the optical density and the gloss of the printed ink will be lower, hence adversely affecting the quality of print. Therefore, it is always recommended that any process ink to be used in offset printing should accept only a moderate or optimal amount of water during print production. The results from the emulsification testing suggests that the overall water accepting capacity of all the inks made from tall oil resin was lower than those made from gum resin, making them suitable for being used for quality offset print production purposes.

Conclusion

The results suggest that tall oil rosin based resin offers a very promising alternative to conventional resin systems. The inks prepared from such resins provide not just comparable rheological properties but superior pigment dispersion and gloss to the final ink, which puts such ink in an advantageous position both from the perspective of manufacturing as well as their usability in lithographic print production. This result is insightful, inks with resin systems having high solvent tolerance although possess good dispersion and gloss properties, often have poor setting times on substrate. But in case of tall oil rosin based resin, a unique advantage can be reported through this work, as the results conclusively suggest that inks made with this resin has good dispersion and gloss properties as well as better setting times and block resistance than gum rosin based resin. Tall oil resin offers a distinct advantage of quick drying yet high gloss properties to the process inks manufactured from it. It can also be inferred from this work that tall oil resin used to make offset printing inks are compatible with the existing varnish system referred to in this work. The inks apart from having good gloss and setting properties also exhibits very good post-print properties like abrasion resistance and block resistance. The inks made with tall oil resin complies with all necessary properties required from sheet-fed offset inks for application in package printing. Further investigation can be conducted regarding naturally sourced materials like tall oil rosin based resin, and their viability over energy cured products in scenarios where regulatory compliance is essential or in manufacturing inks used for food packaging.

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