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Development of Karanja Oil Based Offset Printing Ink in Comparison with Linseed Oil

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Abstract: The conventional offset lithographic printing ink is mainly based on linseed oil. But in recent years, due to stiff competition from synthetic substitutes mainly from petroleum products, the crop production shrinks down to an unsustainable level, which increases the price of linseed oil. Though soyabean oil has replaced a major portion of linseed oil, it is also necessary to develop alternate cost effective vegetable oils for printing ink industry. The present study aims to evaluate the performance of karanja oil (*Pongamia glabra*) as an alternative of linseed oil in the formulation of offset printing ink because karanja oil is easily available in rural India. Physical properties of raw karanja oil are measured and compared with that of alkali refined linseed oil. Rosin modified phenolic resin based varnishes were made with linseed oil as well as with karanja oil and their properties are compared. Sheetfed offset inks of process colour yellow and cyan is chosen to evaluate the effect of karanja oil in ink properties. In conclusion, karanja oil can be accepted as an alternate vegetable oil source with its noticeable effect on print and post print properties with slower drying time on paper. However, the colour and odour of the oil will restrict its usage on offset inks.

Key words: offset printing ink, karanja oil

1 INTRODUCTION

From very first stage of offset ink development, linseed oil has been used as one of the main constituent of offset printing ink formulation[1-2]apart from its principal usage in paints, linoleum, putty and livestock feed from its cake. Linseed oil has experienced a stiff competition from synthetic substitutes mainly from petroleum products and new age plastics. A combined effect of many of these caused production drops and consequently disproportionate increase in price. Due to this, the major share has been captured by soybean oil especially in printing ink industry in the last few years. In Indian context, the use of minor oils in various industrial sections is very much important due to huge import volume of soybean and other oils. To reduce the dependency on import, it is necessary to source out other alternative sources of vegetable oil particularly various minor vegetable oil in India[3]. At the same time recently public awareness to minimize the pollution increase the chance of usage more and more vegetable oil in place of petroleum sources which will help to reduce the volatile organic content (VOC) from printing inks[4-5]. India is producing a significant amount of karanja oil and used mainly as non-edible industrial oil. It is also used as raw material as soap and after sulphonation in the leather tanning industry. The main constrain for more usage of karanja oil in soaps and other industry is its colour and odour[6].

In the present work, raw karanja oil has been taken as an alternative of linseed oil because of its easy availability and low cost to study the feasibility of using karanja oil in offset sheetfed printing ink applications in comparison with linseed oil.

2 MATERIALS AND METHODS

2.1 Materials used

Alkali refined linseed oil and karanja oil was obtained from Viscous Oil and Industries Ltd., Madhya Pradesh, India. Both medium viscosity, medium tolerance rosin modified phenolic resin and long oil linseed isophthalic alkyd

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resin were used from DIC India Ltd., Kolkata, India. Mineral oil distillate used was from Madhusudan Oils Ltd., Kolkata, India and having boiling range of 245-355℃ and aniline point 80℃.

Pigment yellow 12 was used of Sudarshan Chemicals and Industries, Pune, India and Beta blue of SMC Ltd., Ahmedabad, Gujrat, India. Aluminium silicate from BASF Corporation (New Jersey, USA) was used as extender. The additives used were aluminium chelate of Fed Chem Corporation, Cleveland (Ohio, USA); butylated hydroxy toluene of Camlin Ltd., Maharastra, India, polyethylene (PE) wax paste and litho additive from Hexion Corporation, Carpentersville, IL, USA and mixed drier of Co, Mn octoate from Dura Chemicals, Mumbai, India.

2.2 Preparation of varnish[7)]

The vegetable oil was charged in a five-necked one litre glass kettle fitted with a mechanical stirrer, a nitrogen inlet, a thermometer and a condenser, and heated to 140℃. Resin was added, heated to 220℃ and cooked for 30 mins. Distillate was added to form the pregel state and then gelled by adding Al-chelate at 160℃. Butylated hydroxyl toluene (BHT) was added as antioxidant and finally varnish was filtered off. A portion of the pregel material was stored for analysis.

2.3 Preparation of finished ink[8)]

The finished ink was prepared in the laboratory by mixing the ingredients followed by milling with the help of a Laboratory 3-roll mill (Buhler, Switzerland) three times at 22 bar pressure and finished ink was stored for further testing.

2.4 Tests and measurements[9-11)]

The colour of the vegetable oils was measured by Lovibond Tintometer (Lovibond, 2000, U.K.). Viscosity of the vegetable oil was measured by Ford Cup (B4) method at 30℃. Heptane tolerance of the varnish was measured by following the procedure developed in authors' laboratory. In brief, 2 g of varnish was mixed with 2 g of toluene and the mixture was titrated with n-heptane at 25℃ till the mixture becomes cloudy. Volume of n-heptane required was expressed as heptane tolerance.

Viscosity and yield value of varnish and ink were measured by Laray Viscometer (France) at 30℃. Tack of the finished ink was measured at 32.2℃ at 800 rpm with an Inkometer instrument (Thwing Albert, USA) by taking 1 c.c. of the sample. Emulsification behavior of inks was studied with Lithotronic Emulsification Tester (Novamatics, Germany). (Stirrer speed-1200 rpm, Fount Dose rate－8%).

Printing properties of the finished inks were determined by standard methods adopted by the printing ink manufacturing industries. Laboratory prints and setoff on art paper were taken with the help of a Prufbau printing machine (Prufbau, Germany) at 30℃. The optical density of the prints was measured with a Densitometer (D 19C Gretag, Switzerland). Gloss of the prints was measured with Glossometer (BYK Gardner, Sheen Instruments, U.K.) at 75° reflections. The drying property of the prints is compared by taking the prints on both gloss and matt art paper. The time taken by the ink film on paper to dry completely (tack free) was noted as drying time.

3 RESULTS AND DISCUSSION

Comparative properties of the vegetable oils are presented in Table 1 along with the fatty acid composition of each vegetable oil. The inherent property of a vegetable oil is dependent on the fatty acid composition. Karanja oil contains higher percentage of mono unsaturated fatty acid compared to linseed oil. The viscosity of karanja oil is little bit higher due to its raw nature. The free fatty acid (FFA) content of karanja oil is also very high.

Varnish formulation is given in Table 2 whereas varnish properties are presented in Table 3. Varnish-A is produced from linseed oil and Varnish-B is produced from karanja oil. In both pregel and final state, karanja oil is showing higher viscosity and tack, which is mainly due to high FFA content of karanja oil. But the yield value of linseed oil based varnish is higher in final state because of the higher extent of polymerization compared to karanja oil based varnish.

Table 1 Properties of linseed and raw karanja oil used in printing ink

Properties	Linseed oil	Raw Karanja oil
Colour (PRS)	2.0	3.0
*Specific gravity	0.924 ± 0.004	0.931 ± 0.004
*Acid value	0.75 ± 0.03	18.0 ± 0.03
*Viscosity, (s)	22 ± 1	24 ± 1
Iodine value	176.4	89.3
Fatty acid composition (%)		
$C_{16:0}$	6.0	10.5
$C_{18:0}$	3.0	7.2
$C_{18:1}$	17.0	51.4
$C_{18:2}$	14.0	19.2
$C_{18:3}$	60.0	–
$C_{20:0}$	–	3.5
$C_{20:1}$	–	1.4
$C_{22:0}$	–	4.3
$C_{24:0}$	–	2.4

*Values are mean ± SD, n=3

Table 2 Formulation of the varnish prepared from linseed oil and karanja oil

Raw Materials	Varnish A (Based on linseed oil) % (w/w)	Varnish B (Based on karanja oil) % (w/w)
Alkali refined linseed oil	35.0	–
Raw karanja oil	–	35.0
Rosin modified phenolic resin	37.0	37.0
Mineral distillate	26.8	26.6
Al-chelate	0.9	1.1
BHT	0.3	0.3

Table 3 Properties of varnishes prepared from linseed oil and karanja oil

Properties	Varnish A (Based on linseed oil)		Varnish B (Based on karanja oil)	
	Pregel state	Final state	Pregel state	Final state
Laray Viscosity (Pa s)	13.5 ± 0.5	35.0 ± 1.0	19.5 ± 0.5	37.0 ± 1.0
Yield Value ($N\ m^{-2}$)	200 ± 100	1000 ± 200	200 ± 100	300 ± 100
Tack (g M)	9.9 ± 0.2	10.0 ± 0.2	12.3 ± 0.1	12.5 ± 0.1
Heptane tolerance (mL)	6.9 ± 0.1	6.8 ± 0.2	7.0 ± 0.2	7.0 ± 0.1

Pregel state: Before adding gelling agent during preparation of varnish
Final state: the varnish after gelling at appropriate temperature

Values are mean ± SD, n=3

Table 4 Formulation of the printing ink by using different varnishes prepared from linseed oil and karanja oil

Raw Materials	Percent composition (w/w)			
	Yellow		Cyan	
	Ink A (Based on linseed oil)	Ink B (Based on karanja oil)	Ink C (Based on linseed oil)	Ink D (Based on karanja oil)
Varnish A	70.0	–	66.7	–
Varnish B	–	70.0	–	66.7
Alkyd	5.0	5.0	5.0	5.0
Yellow Pigment	12.5	12.5	–	–
Cyan Pigment	–	–	18.0	18.0
PE wax paste	3.0	3.0	3.0	3.0
Litho additive	0.5	0.5	0.5	0.5
Antioxidant	0.5	0.5	0.8	0.8
Mixed Drier	1.0	1.0	1.0	1.0
Mineral Distillate	7.5	7.5	5.0	5.0

Higher yield value signifies that the ink has the proper structure to withstand the shear force generated between the inking rollers of the machine during printing. If the structure breaks easily, it will be difficult to get the proper ink transfer, which will affect the print quality. Heptane tolerance is an important factor to evaluate the printing prop-

Table 5 Rheological properties of inks prepared from linseed oil and karanja oil of two different colours

Properties	Yellow		Cyan	
	Ink A (Based on linseed oil)	Ink B (Based on karanja oil)	Ink C (Based on linseed oil)	Ink D (Based on karanja oil)
Pigment Dispersion (μM)	10 ± 2	11 ± 1	10 ± 2	11 ± 1
Laray Viscosity, (Pa s)	24.0 ± 1.5	25.5 ± 1.0	22.0 ± 1.5	20.0± 1.0
Yield Value, (N m^{-2})	1700 ± 200	900 ± 200	1300 ± 200	800 ± 100
Tack, (g m)	9.6 ± 0.1	10.1 ± 0.1	9.5 ± 0.1	9.8 ± 0.1
Flow, (m)	0.12 ± 0.005	0.15 ± 0.005	0.14 ± 0.005	0.15 ± 0.005
Lithotronic Properties				
Tq Start, (mJ)	504 ± 30	488 ± 25	504 ± 30	488 ± 25
Δ Tq ,(mJ)	52 ± 5	30 ± 7	52 ± 5	30 ± 7
Emulsification capacity EC (%)	70 ± 2	85 ± 2	90 ± 2	90 ± 2

*Values are mean ± SD, n=3

Table 6 Print and post-print properties of the inks (Prufbau/Gloss Art Paper (130 GSM) printed at 30℃)

Properties	Different Inks			
	Yellow		Cyan	
	Ink A (Based on linseed oil)	Ink B (Based on karanja oil)	Ink C (Based on linseed oil)	Ink D (Based on karanja oil)
*Optical Density	1.72 ± 0.01	1.74 ± 0.02	2.29± 0.01	2.29 ± 0.02
Gloss (Glossometer/75° reflection)	82.0	87.0	76.0	79.0
Print Setting (100 - Best; 0-worst)	70	70	75	70

*Values are mean ± SD, n=3

Table 7 Drying and skinning properties of the finished ink

Properties	Different Inks			
	Yellow		Cyan	
	Ink A (Based on linseed oil)	Ink B (Based on karanja oil)	Ink C (Based on linseed oil)	Ink D (Based on karanja oil)
Substrate Drying Time, (mins) (Gloss Art paper/Matt art paper)	585/585	685/685	300/360	570/600
Skinning Time, (days)	>7	>7	1-2	4-5

erties of the finished ink. Heptane tolerance of karanja oil based varnish is slightly higher which may help to produce ink with better gloss. But the colour of karanja oil based varnish is in darker side along with a pungent smell compared to linseed oil based varnish.

Two inks of process colour yellow and cyan are made with both linseed and karanja oil based varnishes. The ink formulations are given in Table 4. The dark colour of karanja oil makes the masstone of yellow ink dirtier compared to linseed oil. At the same time, both yellow and cyan inks based on karanja oil are having pungent odour compared to linseed oil.

A good combination of rheological properties of printing ink will help to produce clear and sharp printed image with good dot reproduction. Rheological properties of the inks presented in Table 5 shows that karanja oil based ink is having more or less comparable viscosity and tack with higher flowablility with respect to linseed oil in both yellow and cyan. Higher flowability helps to transfer the ink from ink duct to roller of the machine during printing. The difference in viscosity and yield value between yellow and cyan inks is due to difference in formulations of the two inks. Generally in yellow, pigmentation level is kept at lower level (i.e at 12.5%) compared to cyan (i.e 18.0%) in order to achieve good colour balance with proper print density during printing. As a consequence the varnish content in yellow is becoming higher which gives higher yield value compared to cyan.

Emulsification uptake capacity of the printing ink is an important parameter during final offset printing. In the present study the emulsification capacity is expressed through the measurement of torque (Tq) value. The lower delta torque value means better emulsification property. Table 5 shows that karanja oil based ink is showing almost similar water uptake value with lower delta torque value which means that karanja oil based ink will form the stable emulsion with water during offset printing compared to linseed oil based ink.

Print and post print properties of the inks based on optical density, gloss and setting properties are presented in Table 6. Optical density and setting of all the inks is comparable which means that the runnability of both the inks in machine is more or less same. Gloss of karanja oil based ink is higher than that of linseed oil based ink because the extent of polymerisation is less in karanja oil than linseed oil.

Drying time i.e. the time taken to make a hard dried ink film (tack free) is higher in case of karanja oil based ink as it is having mainly mono-unsaturated fatty acids (Table 7). Skinning times of the karanja oil based inks are also higher than linseed oil based ink which indicates that karanja oil based ink will remain open (i.e. skin free) for a longer period of time without forming any skin in ink duct of the printing machine. However, on paper after printing, karanja oil based ink will take more time to fully dry, hence it may hamper the post print workflow process such as folding, cutting, binding etc of the printed matters.

From the whole evaluation, it can be stated that karanja oil is giving advantages with good rheological and print properties (specially gloss), which can help to reproduce a superior quality of printed specimen with less hazards in the runnability in the machine. The effect of slower drying rate of karanja oil can be taken care of in the final formulation with the dosage adjustment of antioxidant and drier. The darker colour and pungent smell of raw karanja oil can make its usage very restricted in sheetfed offset inks for good quality printing jobs especially in lighter colour and tint.

4 CONCLUSION

The darker colour and pungent smell of raw karanja oil can be compensated by using it for making of low quality, cheaper grade offset ink (where colour and odour are not very critical) and can be a suitable area for karanja oil as a replacement of linseed oil. A further work for usage of raw karanja oil in offset book black printing ink based on gilsonite or bitumen resin can generate a more purposeful new application area of this oil.

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