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MODIFYING THE DRYING PROPERTY OF RUBBER-SEED OIL.

A. N. ANOZIE and A. T. OGUNSANYA

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ABSTRACT

Rubber-seed oil, a semi drying oil, was modified by boiling and blowing process in the presence of a drier to enhance its drying property. The oil boiling and blowing process was carried out with variation in temperature, time and type of drier used. The levels of unsaturation of the oil in the natural and modified states were determined by the iodine value using Wij's method. The effects of temperature, time and type of drier used on iodine value and viscosity of the modified oil were examined. It was found that low iodine value and high viscosity of the boiled and blown oil enhanced the drying property of the oil and these two parameters were used to select oil samples for putty making. Putty was prepared using the selected oil samples and whiting. The best operating conditions (local optimum) for the oil modification process, which gave the best putty, were determined by testing the quality of the putty in terms of adhesion, cohesion, drying time and colour. The local optimum conditions for the oil modification process were found to be boiling and blowing with lead grains either at 150°C for 3 hours or at 200°C for 2 hours.

KEYWORDS: Rubber-seed oil, boiling, blowing, drying property, putty.

INTRODUCTION

The rubber tree (Hevea brasiliensis) is one of the most important economic trees in the tropics. It is found predominantly in the tropical rain forest zone of South-East Asia, South America and West and Central Africa (Enabor, 1985). Today, large rubber tree plantations exist in many southern states of Nigeria (Amobi and Nzekwe, 1985) .The tree has long been cultivated principally for its latex. About three decades ago falling latex prices, due to competition with synthetic rubber, became a set back in the cultivation of rubber tree. Presently, interest in the rubber tree has risen again not only because of the better prices of latex in the world market but also because of special properties of the rubber-seed oil (Obasi and Hymore, 1994).

Various authors have reported that rubber-seed oil could be used for the manufacture of alkyd resins, paints, printing inks, putty and fat-liquor (Adefarati, 1985; Uzu et al. 1985; Bangaruswany and Obunukut, 1985). This is because the oil has a relatively high iodine value which determines the ability of oil to absorb atmospheric oxygen to form a transparent film or resin .The reaction of the oil with the oxygen in the air is known as autoxidation. Autoxidation takes place when the temperature is high enough and even at ordinary atmospheric temperature when the reaction is promoted by light and photosensitizers and by certain micro-organisms (Eckey, 1954). The iodine value of oil is the measure of the degree of unsaturation of the fatty acids in the oil. For example, rubber-seed oil and soya-bean oil are classified as semi-drying oils while linseed oil is classified as a drying oil. Semi-drying oils have iodine values usually from 120-140 while drying oils have iodine values from 160-205. Secondly, semi-drying oils contain little unsaturated fatty acids with three double bonds while drying oils contain quite a percentage of such acids. Thirdly, semi-drying oils when exposed to air take very much longer time to dry but have better colour retention and are less coloured than those of drying oils (Morgans, 1969)

It is possible to modify oil by a technical process to obtain oil with improved drying property. Several methods of modifying oils to improve their drying properties exist. These methods include: boiling, blowing, dehydration, isomerisation and fractional separation of oils (Apps, 1961; Payne, 1965; Kroschwitz and Howe-Grant 1998, Obasi and Hymore, 1994). By far, the two commonest methods are boiling and blowing. Boiling involves heat polymerization or bodying of oils by heating to higher temperature in the presence of driers. The most conspicuous changes during bodying are an increase in viscosity of the oil and decrease in iodine value. Blowing involves oxidation of the oil with air either at ordinary or moderate temperatures with or without driers. A stream of air or oxygen is introduced below the surface of the oil. This produces an oil of higher viscosity accompanied by increase in specific gravity, refractive index, free acid content and decrease in iodine value (Apps, 1961).

Despite the local availability of rubber seeds in the country, no attempt has been made to produce and/or modify the oil for commercial and industrial purposes. There is no doubt that the local sourcing of our industrial raw materials like drying oils will save foreign exchange for the country. It will reduce the price of products manufactured from such raw materials, for example putty, and create job opportunities. Putty is made by mixing whiting with boiled linseed oil, which sets by autoxidation and by formation of calcium salt. Whiting is pure, finely divided calcium carbonate prepared by wet grinding and levigating natural chalk. There is abundance of calcium carbonate in Nigeria. Linseed oil is not produced in Nigeria but rubber-seed oil can be boiled and blown and used as a substitute in the preparation of putty and other products.

In this study, the drying property of rubber-seed oil was modified by simultaneous boiling and blowing process in the presence of a drier so as to enhance its drying property. The double treatment of boiling and blowing rather than just boiling or blowing was given to the rubber-seed oil to ensure that adequate drying

A. N. ANOZIE, Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife - Nigeria
A. T. OGUNSANYA, Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife - Nigeria

property was conferred on it. The iodine values of the oil before and after boiling and blowing treatment were determined using Wij's method. The effects of temperature, time and drier type on iodine value and viscosity of the modified oil were evaluated and used to select oil samples with enhanced drying property. Putty was prepared using the selected oil samples and whiting. The best operating conditions (local optimum) for the oil modification process was determined by testing the quality of the putty in terms of adhesion, cohesion, drying time and colour.

MATERIALS AND METHODS

1. Materials

The following materials were used:
(i) Rubber-seed oil
(ii) Driers. The oil driers used and their percentage by weight of the oil are as follows: manganese dioxide-1%, lead grains-2% and cerium sulphate-1%.
(iii) Whiting

2. Major Equipment

(i) Fabricated vessel
A metal vessel, 20cm high, 6cm internal diameter and 3mm thick was fabricated and used for the boiling and blowing operation.
(ii) Laboratory equipment
This comprised of the following: burette, pipette, beakers, conical flasks, thermometer, an air compressor and a hot plate with temperature regulator.

3. Procedure

The following methods were used:

(i) Oil boiling and blowing process

The experimental set up is shown in Fig.1. About 20g of rubber-seed oil was weighed into the fabricated metal vessel. The required percentage by weight of drier was weighed and added to the oil. The metal vessel with oil was heated on a hot plate to the desired temperature. Air was blown through the oil in the metal vessel by means of a compressor. After each boiling and blowing time interval, the oil was poured into a glass container and corked to avoid air drying by oxidation. The physical observation of colour and viscosity were recorded. The iodine value of the dried oil was determined. The boiling temperature was varied from 30°C (room temperature) to 200°C. The time of boiling and blowing was varied from 1 to 3 hours.

(ii)Determination of iodine value

The official methods of analysis (AOAC, 1984) were used for the determination of iodine value of natural rubber-seed and boiled and blown rubber-seed oil samples. About 0.3g of oil was weighed into a glass, stoppered flask and 15ml of carbon tetrachloride added. The flask was shaken to completely dissolve the oil. 250ml of Wij's reagent was carefully added using a pipette. The flask was then stoppered and shaken gently and stored in the dark for 30 minutes. 20ml of 15% potassium iodide solution and 100ml of freshly distilled water were added. Titration was carried out with 0.1N sodium thiosulphate solution using 1ml starch indicator with vigorous shaking. The above procedure was repeated for the blank preparation except that the oil was not added. Experiments were performed in duplicates. The iodine value was calculated as follows:

$$\text{Iodine Value} = \frac{(\text{ml blank-ml sample}) \times N \times 0.12692 \times 100}{\text{Weight of sample of oil (g)}} \quad ....(1)$$

where N = normality of the sodium thiosulphate solution used = 0.1

(iii) Preparation and testing of putty

Putty was prepared by mixing 82% whiting and 18% boiled and blown rubber-seed oil. A few drops of solvent were added to aid mixing and improve pliability. The putty was spread lightly on a ceramic surface and allowed to dry. The drying time was recorded and the colour, adhesion and cohesion behaviours of the putty were observed.

RESULTS AND DISCUSSIONS

Table 1 shows the operating conditions and results of the oil boiling and blowing process and the iodine value of natural rubber-seed oil.

1. Iodine Value of Natural Rubber-Seed Oil

The iodine value of the natural rubber-seed oil, oil sample 0 in Table 1, is 132.33. This result is close to that of 130.2 reported by Assuncao et al (1984). The result confirmed that rubber-seed oil is semi-drying oil. The iodine value of natural oil is a useful index in determining whether the oil is drying, semi-drying or non-drying. It measures the degree of unsaturation which is needed for chemical reaction between the oil and oxygen and between the oil and drier.

2. Boiled and Blown Rubber-Seed Oil

The modified rubber-seed oils are oil samples 1-10 in Table 1.

(i) Iodine Value

The boiling and blowing operations in the presence of driers and at elevated temperatures reduced the iodine value of the oil due to polymerization and autoxidation reactions, which had occurred, with the consequent reduction in unsaturation of the oil. Therefore the lower the iodine value of the modified oil, the greater the extent of polymerization and autoxidation reactions that had occurred and the better the improvement in the drying property of the oil.

The iodine value of oil samples 6 and 7 showed that temperature was the most important factor in boiling and blowing of oils. The iodine value of oil sample 1 showed that the presence of a drier was very necessary. The iodine value of oil samples 2, 3 and 4 showed that lead grains and manganese dioxide were good driers but that cerium sulphate was not a good drier and should not be used at all.

The disparity in titre values could be attributed to differences in rates of reaction with Wij's reagent in the dark for 30 minutes, due partly to the differences in the intensity of light and the various accuracies of the measured quantities like volume of solutions. Iodine values were not determined for samples with high viscosities obtained at higher temperatures and longer times of boiling and blowing, instead the drying

Table 1: Operating Conditions and Results of the oil boiling and blowing process

Sample	0*	1	2	3**	4	5**	6	7	8**	9**	10
Weight of oil(g)	-	20.00	19.703	16.970	21.083	36.020	20.041	19.150	23.721	25.133	250.010
Drier	-	none	MnO2	Pb grains	$Ce(SO_4)_2.4H_2O$	Pb grains	MnO_2	Pb grains	Pb grains	Pb grains	Pb grains
Weigh of drier(g)	-	-	0.197	0.342	0.210	0.736	0.200	0.387	0.477	0.503	0.500
Temperature (°C)	-	150	150	150	150	30 (Room Temp)	30 (Room Temp)	30 (Room Temp)	200	200	275
Total time of boiling and blowing (hrs)	-	2	2	2	2	3	2	2	2	3	3
Colour of oil (Observation)	Very light brown	Very light brown	Dark brown	Reddish brown	Light brown	Reddish brown	Dark brown	Reddish brown	Reddish Brown	Reddish brown	Reddish brown
Viscosity of oil (Observation)	(Reference)	Slight increase	Slight increase	Slight increase	Slight increase	Marginal increase	Reduced	Reduced	Marginal increase	Marginal increase	Almost solid
Weight of oil tested with Wij's reagent (g)	0.301	0.300	0.310	0.281	0.300	-	0.300	0.302	-	-	-
Volume of sodium thiosulphate solution used for titration (ml)	32.05 32.00	45.00 44.20	46.20 46.15	50.05 50.07	45.42 45.38	-	39.93 39.94	39.96 39.94	-	-	-
Iodine Value	132.21 132.45	77.84 80.81	70.42 70.22	60.30 59.76	76.07 75.82	-	99.294 99.998	98.510 98.174	-	-	-

*Natural Rubber-seed oil
**Modified oils used for putty making
Note: ml sodium thiosulphate solution for blank preparation = 63.40

Table 2 : Results of tests to determine quality of putty

Oil samples	Weight of oil (g)	Weight of $CaCO_3$(g)	Putty			
			Adhesion	Cohesion	Drying time (min)	Final colour
3	0.604	2.752	Fair	Fair	60	Grey
5	0.614	2.797	Good	Good	48	Light grey
8	0.713	3.248	Good	Good	45	Light grey
9	0.687	3.116	Poor	Poor	45	Dark grey
10	0.660	3.029	Poor	Poor	45	Light brown

capacities of these samples were assessed by observing their viscosities.

(ii) Viscosity

Viscosity increased with increase in temperature of boiling and blowing when time of operation and drier type remained constant .Viscosity also increased with time of operation when temperature and drier type remained constant. The increase in viscosity with temperature and time of operation during boiling and blowing could be attributed to heat polymerization or bodying of oil in the presence of a drier and autoxidation of oil in the presence of oxygen from the air. A high viscosity would imply a high degree of bodying and autoxidation of oil and hence a better drying property. The most remarkable increase in viscosity was noticed with lead grains, which had proved the best of the three driers considered.

Oil samples 6 and 7 prepared at room temperature did not achieve the desired result. The final oil was of a lower viscosity and the driers simply settled down at the bottom of the vessel, leaving brown oil at the top. This confirmed the fact that elevated temperature is necessary to achieve an increased viscosity. Oil samples 5, 8 and 9 had increased viscosity and were not subjected to solidification on exposure to the atmosphere whereas oil sample 10 on mere exposure to air for upwards of five minutes resulted in solidification.

From the foregoing, it was rightly deduced that boiled and blown oil sample with low iodine value and/or high viscosity would have enhanced drying property. Hence, oil samples 3, 5, 8, 9 and 10 in Table 1 were considered to have enhanced drying property. These samples were prepared with lead grains.

3. Testing the quality of putty

The selected oil samples 3, 5, 8, 9 and 10 in Table 1 were used in the preparation of putty as described under methodology. Table 2 shows the results of the tests carried out to determine the quality of putties. Putties made with oil samples 5 and 8 had both good adhesion and good cohesion. In terms of colour, putty made with oil samples 5 and 8 gave the best color, which was grey. The drying time for the putty samples ranged between 45 minutes and 1 hour. Putty made with oil sample 5 had a drying time of 48 minutes while that made with oil sample 8 had a drying time of 45 minutes. The difference in drying time between these two samples was negligible and these two samples were judged to be the best. Oil samples 5 and 8 were produced at the following operating conditions in the boiling and blowing process: temperatures of 150°C and time at 3 hours (oil sample 5) and temperature of 200°C and time of 2 hours (oil sample 8). These operating conditions represent the local optimum operating conditions.

CONCLUSION

The drying property of rubber-seed oil, semi-drying oil, was successfully modified by boiling and blowing process in the presence of lead grains as a drier. Boiling and blowing reduced the iodine value and increased the viscosity of the oil, both an indication of improvement in drying property. Putty of good quality was also successfully prepared using the boiled and blown rubber-seed oil. The best putties were those which were prepared with oil samples 5 and 8. Oil samples 5 and 8 were boiled and blown at the following conditions: temperature of 150°C and time of 3 hours (oil sample 5) and temperature of 200°C and time of 2 hours (oil sample 8). These conditions represent the best operating conditions (local optimum) for the oil boiling and blowing process. The final choice between these two conditions will now depend solely on the economics involved which would mean choosing between providing compressed air for blowing the oil for as long as 3 hours and the provision of a high temperature at 200°C. It is expected, however, that either of these two alternatives would be better economically than the use of imported linseed oil in the preparation of putty.

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