

Full Length Research Paper

Effect of presence of free fatty acids on the drying of oil/drying catalysts mixtures

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Free fatty acids are usually generated spontaneously in oils either by action of enzymes inadvertently entrained during storage or mineral acids inherited from the refining process. The study investigated the effect of the presence of excess fatty acids on the drying/curing behaviour of drying oil admixed with drying catalysts. The oxygen absorption behaviours of Linseed oil (LSO) and rubber seed oil (RSO) on one hand, and that of their corresponding free fatty acids, namely linseed fatty acids (LSA) and rubber seed fatty acids (RSA) on the other hand were first compared followed by drying tests of same samples using the set-to-touch method. Results obtained showed the following order of oxygen absorption behaviour: LSA>LSO>RSA>RSO. Although oxygen absorption is a stage subsequent to drying process, the drying behaviour, however, did not follow the same trend with the oxygen absorption pattern. Whereas the oils/drier mixtures underwent drying between 3 and 4 h after they were casted as thin films, the fatty acids did not at all even in presence of varying concentrations, up to maximum of 50 wt, % of the curing agent. Therefore, the presence of free fatty acids in drying oils is assumed to be capable of hampering the curing of the latter. Hence, it is recommended that drying oils intended as oleoresinous binders for surface coatings be refined so as to remove or reduce to the barest minimum of their free fatty acids content in order to obtain products with optimum drying rate at reasonable time period.

Key words: drying oil, free fatty acids (FFAs), oxygen absorption, drying catalyst, surface coating.

INTRODUCTION

Oil, as used in this context, refers to the triglycerides of plants or animal origin and was obtained from the chemical interaction of glycerol with three molecules of fatty acids (Equation 1). The term "oil" is normally used interchangeably with fat (Ibemesi, 1992; Ahmad et al., 1996). However, strictly speaking, oils are triglycerides that are liquid at room temperature while fats are those that are solid or semi-solid under the same conditions. This difference in their physical conditions is attributed to the type of fatty acids composition predominant. Fats are composed of mostly saturated fatty acids while oils are formed from mostly unsaturated fatty acids. On the basis of relative distribution of these two categories of fatty acids, a triglyceride is classified as non-drying, semi-drying or drying (Iyayi et al., 2008; Ejikeme and Ibemesi, 2007), which refers to their susceptibility to absorb

oxygen from atmosphere and react with it to form a tough and elastic solid web ("cross-linked" product) capable of providing weather-resistant protective film. This reaction is the essence of curing and is known as "oxidative polymerization", or simply drying. This is the reason why the drying oils are used as oleo-resinous binders in oil-based varnishes, lacquers or paints. The mechanism of drying is due to complicated physico-chemical processes, but generally believed to involve a combination of evaporation of solvent (volatile organic liquid or water, depending on the type of formulation) as well as reaction of the unsaturated chains of the triglycerides with atmospheric oxygen. The rate of evaporation of the solvent from the paint is a function of the thickness of the layer, temperature, the nature of the drying oil and the solvent, and of the presence of other components, namely pigments and additives (Hajek and Krejcar, 1967).

Among such additives, one type which plays a key role in the drying process is the drying catalyst or drier. Driers are soaps/ salts obtained via the reaction between organic acids, such as linoleic, oleic, naphthenic acids, to

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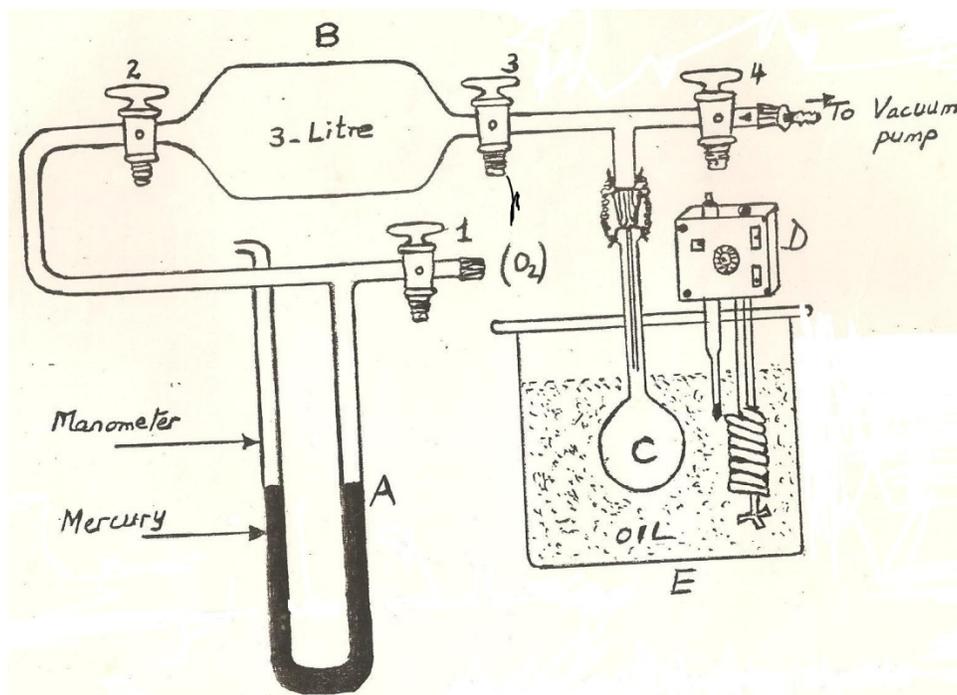


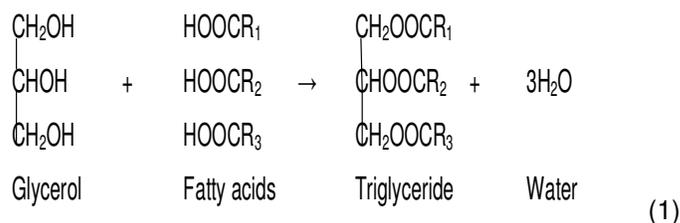
Figure 1. Oxygen absorption apparatus (Glass manometer assembly).

mention but a few, and metals such as cobalt, lead, manganese, calcium, etc. The catalytic action of these driers is due only to the metallic portion, while the organic portion of the salt serves merely to solubilise the metal in the binder. Film formation in the presence of driers is marked by a shortened induction period, an increase in rate of oxidation, formation of film at a lower oxygen content of total oxygen during subsequent aging (Greenwald, 1948). The mechanism involved is believed to proceed via a number of reaction pathways each of which demonstrates a simple cycle of valency changes, as described by the sequence (scheme A) subsequently.

Free fatty acids (FFAs) are spontaneously generated from oils while on storage because of hydrolysis. This phenomenon is what is responsible for the so called oil rancidity. The agents of hydrolysis are either enzymes or certain chemical species which inadvertently came in contact with the oils during storage/ processing. The amount of FFAs are evaluated in terms of the parameter known as "Acid number", defined as the number of milligrams of potassium hydroxide required to neutralize the alkali reactive groups in one gram of oil under the conditions of test (ASTM, 1973). From literature, this piece of work seems to be the first attempt of a systematic study on the effect of the presence of FFAs on the curing behaviour of drying oils. This knowledge gap is, therefore, the thrust of the present paper.

The procedure employed in the present investigation devolves into two parts, namely: the comparison of the oxygen absorption capacity of free fatty acids and corresponding oils as first part, and their drying behaviour

when spread as a thin film on suitable substrates. The equipment used for the measurement of oxygen capacity was a locally constructed manometer assembly (Igwebike and Ibemesi, 1991) (Figure 1). Connected to a reaction vessel is a delivery tube by which the oxygen from a supply source comes in contact with the sample, and as the oxygen is consumed due to the reaction, the rate is monitored simultaneously by the movement of mercury contained in the manometer.

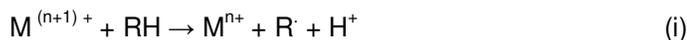


Where R_1 , R_2 and R_3 represents hydrocarbon chains, which may/may not contain unsaturation. The degrees of unsaturation in the chains determine the classification of the triglyceride into non-drying, semi-drying and drying. In some instances, all the Rs are the same structurally but usually they are different.

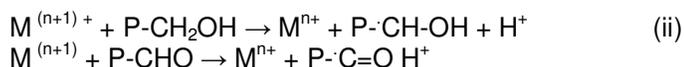
MECHANISM OF DRIER ACTION IN CURING A DRYING OIL (SCHEME A)

Direct action of a metal ion with a hydrocarbon/polymer (RH) chain in the early stage of autoxidation (Mraz and

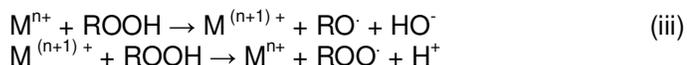
Silver, 1965):



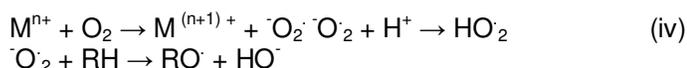
Interaction of metal ions with hydroxyl and aldehyde groups (coming from the products of autoxidation):



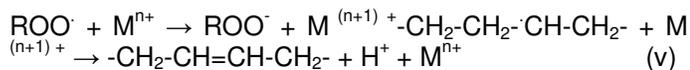
Decomposition of hydroperoxides with metal ions:



Direct interaction of transition metals with oxygen leading to formation of loose complex between metal catalyst in a lower state of valency and oxygen, in the course of which the metal ion is oxidized to a higher valency state:



The metal ions may react as antioxidant by destruction of peroxy radicals:



MATERIALS AND METHODS

Sample collection and treatments

Linseed oil (LSO) was obtained in a refined state and was a product of George Rowny and Company Limited, England. It was used as supplied. Rubber seed oil (RSO) was solvent extracted from the rubber seeds gathered from the farm of the Faculty of Agriculture, University of Nigeria, Nsukka using cold process technology. Before usage, the extracted oil was alkali-refined and afterwards bleached using Fuller's Earth (a product of Fullmont Limited, England, supplied by Lever Brothers Nigeria Limited, Lagos). The corresponding fatty acids, namely linseed fatty acids (LSAs) and rubber seed fatty acids (RSAs) respectively were prepared from their oils and used. Cobalt and lead naphthenates, obtained from Morgan Paints, Nigeria Limited, Enugu, served as drying catalysts. Oxygen (99.80 to 99.99%) purchased from Niger Gas Nigeria Limited, Emene, near Enugu, Nigeria, was used.

Extraction and refining of RSO

"The cold solvent extraction procedure (M.N. Igwe, Undergraduate Project, University of Nigeria, Nsukka, 1986; C.D. Igwebike, Masters Dissertation, University of Nigeria, Nsukka, 1989) was used as absence of electricity would not permit the use of the popular technique based on Soxhlet apparatus". The oil-bearing seeds which have been oven-dried to constant weight were ground to fine meal using motorized grinder. The resulting meal was fed into a glass column (113 cm in length and 7.3 cm in diameter) equipped with a tap, in the shape of ordinary titration burette, up to 100 cm of its length. The exit of the column was packed with sufficient glass wool as a sieve to permit the extracted oil only to pass through. Petroleum ether

(boiling point, 60 to 80°C) was poured into the column in order to saturate the meal with a solvent head over the soaked meal. The top of the column was then covered with a glass Petri-dish to minimize the loss of solvent through evaporation while the set up is kept under observation at room temperature for 24 h. At the end of the period, the tap was opened to collect the oil/solvent mixture. This procedure was repeated until the exiting oil/solvent mixture became colourless and the meal itself whitish indicating maximum extraction of the oil. The oil was separated from the solvent via distillation taking advantage of the respective varied boiling points of the oil and solvent.

The resulting oil was alkali-refined according to method of Cocks and Rede (1966). The resulting oil was then bleached as follows: A known weight of the oil was mixed with Fuller's Earth (15 wt. % based on oil) in a 500 ml round-bottom flask equipped with a side neck connected to a vacuum pump. The flask with its contents was immersed in an oil bath maintained at a temperature of 80°C, and under vacuum. The mixture was stirred at intervals by swirling the flask manually for a period of 40 min. At the end of this bleaching period, the oil/Fuller Earth's mixture was filtered hot under vacuum with the aid of Buchner Funnel. The used Earth was cast off while the oil was reserved for subsequent analysis.

Preparation of FFAs

The oil was first saponified according to standard procedure (Unilever, 1964; Kirk-Othmer, 1965) to obtain its soap. Hot solution of the soap prepared with de-ionized water was acidified with 30 wt. % sulphuric acid while the solution was gently heated. Fatty acids immediately collected on top of the solution, being less dense than the aqueous base, and were separated apart by means of separating funnel. The fatty acids were then washed several times with water until the effluent (wash) water tested neutral to blue litmus paper, indicating complete removal of the mineral acid, sulphuric acid. The acid number of the neutral FFAs was determined (ASTM, 1973).

Oxygen absorption measurements

Oxygen absorbed in the course of autoxidation of the oils of linseed and rubber seed and their corresponding fatty acids were monitored manometrically at ten minutes intervals at room temperature using five grams of each oil/fatty acid, 0.5% and 0.05 wt.% (representing amounts empirically established as optimum for maximum efficiency) of lead and cobalt naphthenates, respectively as driers. The actual amounts of driers weighed in order to give the aforementioned percentages of metals in the samples were calculated using the relationship stated subsequently (Equation 2).

$$\text{Amount of drier} = \text{weight of sample} \times \frac{\% \text{ of metal required}}{\% \text{ of metal in drier}} \quad (2)$$

The oxygen absorption characteristic of each sample was studied using the set up shown in Figure 1.

The reaction of the sample with the inlet oxygen results in the depletion of the oxygen which was monitored at intervals of ten minutes for a three-hour period for all the samples by the measurement of mercury height. At the end of the experiment, the weight of the sample, after it has been cooled to room temperature, was recorded to obtain any gain in weight due to oxygen absorption. The reproducibility of these measurements was established by repeated experiments on randomly selected samples.

Table 1. Pressure (P cm Hg) and Moles (n) of unreacted oxygen for different oils and fatty acids, respectively.

Time (min)	LSO		RSO	
	P	n x 1000	P	n x 1000
0	14.1	22.78	14.1	22.78
10	13.9	22.46	14.1	22.78
20	13.5	21.81	13.9	22.45
30	13.1	21.17	13.7	22.13
40	12.9	20.84	13.4	21.64
50	12.5	20.20	13.1	21.16
60	12.3	19.88	12.9	20.83
70	12.1	19.55	12.7	20.51
80	11.7	18.91	12.5	20.19
90	11.5	18.59	12.2	19.70
100	11.3	18.26	12.0	19.38
110	11.1	17.94	11.7	18.89
120	10.9	17.62	11.5	18.57
130	10.7	17.30	11.3	18.24
140	10.7	17.30	11.1	17.92
150	10.5	16.97	10.9	17.60
160	10.4	16.81	10.8	17.44
170	10.3	16.65	10.7	17.27
180	10.1	16.33	10.5	16.95

Drying/ Curing procedure

Oil/driers mixtures were first autoxidised in the Oxygen Absorption Apparatus (Figure 1) resulting in the product which, hereafter, was termed "curing agent" which also served as reference samples. This curing agent was then added to FFAs of linseed and rubber seed, respectively in various amounts to give 0, 10, 20, 30, 40, and 50 wt. % concentration in the FFAs. Both the reference and FFAs samples were cast as thin films on casting surfaces described subsequently. Casting surface areas (1.5 by 7 cm) were tapped off on clean glass plates according to the number of samples. The thicknesses of films were roughly estimated by the measure of thickness of the layers of tape sheets used to create the casting areas. After casting, the liquid mixtures were levelled uniformly by use of gliding glass slides. The cast films were monitored for surface drying at room temperature by set-to-touch method (ASTM, 1973). In this method, a film is set-to-touch when it shows a tacky condition, but none of it sticks to the finger.

RESULTS

The results of oxygen absorption measurements are presented in Tables 1 and 2 for the calculation of moles of oxygen absorbed. The number of moles of oxygen (n) present at any interval was calculated from manometric height or oxygen pressure, P using the ideal gas relation (Equation 3).

$$PV = nRT \quad (3)$$

Where,

P = Pressure of oxygen

V = Volume of the entire system (approximately 3.022 L).

The volume of the system was assessed from the volume of water required to fill the various parts of the system with water including the connecting rubber tubing.

R = Gas constant (0.08205 L atm. /mol K)

T = Temperature of oxygen gas (30 °C)

The change in the number of moles of oxygen absorbed (Δn), which indicates the number of moles of oxygen absorbed with time was calculated from Equation 4.

$$\Delta n = n_0 - n_t \quad (4)$$

Where,

n_0 = moles of oxygen present initially (at $t = 0$)

n_t = moles of oxygen present after a time interval, t.

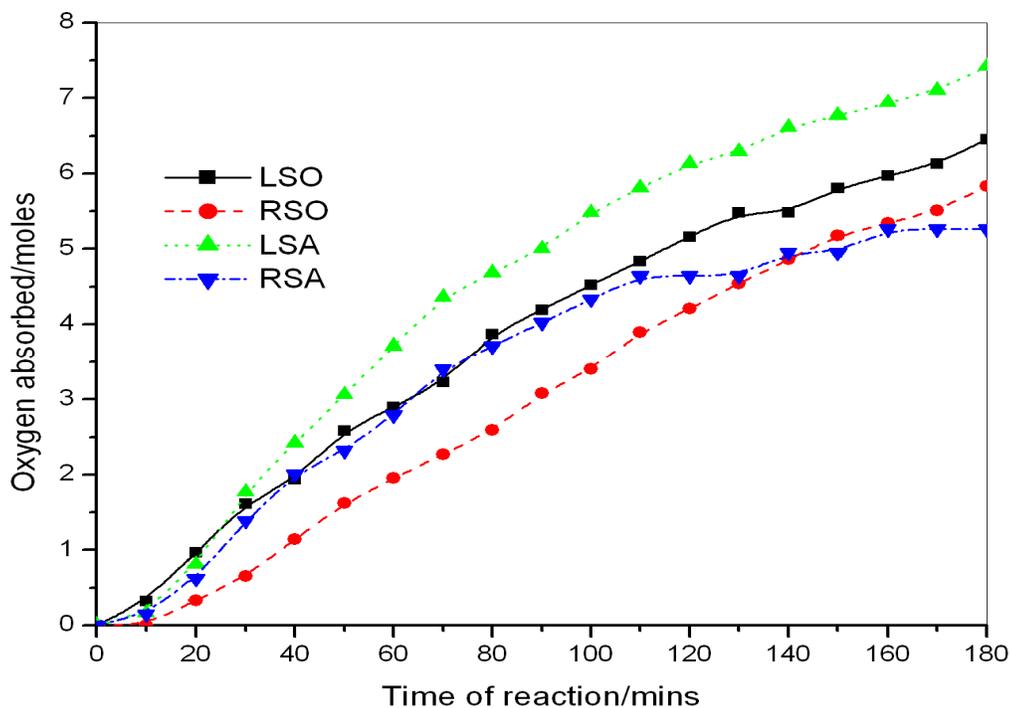
The results showing moles of oxygen absorbed by individual oils (LSO and RSO) and the fatty acids counterparts are compared as shown graphically in Figure 2.

DISCUSSION

As seen from the result in Figure 2, it is observed that the order of oxygen absorption is: LSA>LSO>RSA>RSO. This indicates that LSA absorbed oxygen the most followed by LSO, then RSA and RSO as the least. Both LSO and RSA show oxygen absorption patterns which are quite close during the period from 0 to 100 min, after which the profile for RSA declined markedly. In general, both LSA and LSO show the highest oxygen absorption

Table 2. Pressure (P cm Hg) and moles (n) of unreacted oxygen for the different fatty acids.

Time (min)	LSA		RSA	
	P	n x 1000	P	n x 1000
0	14.1	22.78	14.10	21.83
10	14.0	22.62	14.00	21.68
20	13.6	21.97	13.70	21.21
30	13.0	21.01	13.20	20.44
40	12.6	20.36	12.80	19.82
50	12.2	19.72	12.60	19.51
60	11.8	19.07	12.30	19.04
70	11.4	18.42	11.90	18.42
80	11.2	18.10	11.70	18.12
90	11.0	17.78	11.50	17.81
100	10.7	17.30	11.30	17.5
110	10.5	16.97	11.10	17.19
120	10.3	16.65	11.10	17.19
130	10.2	16.49	11.10	17.19
140	10.0	16.17	10.90	16.88
150	9.9	16.01	10.90	16.88
160	9.8	15.84	10.70	16.57
170	9.7	15.68	10.70	16.57
180	9.5	15.36	10.70	16.57

**Figure 2.** Plots of change in oxygen absorbed vs. time for pure oils and corresponding fatty acids.

capacity. The higher oxygen absorption capacity of linseed FFAs/oil than the RSA and/or RSO is attributed to relatively high preponderance of unsaturated fatty acids

in the former compared to rubber FFAs/oil. Looking at the absorption profile of a given oil relative to its FFA (for example, LSO with LSA or RSO with RSO), it is seen that

the fatty acids demonstrate greater affinity for oxygen than the parent oils. The reason for the higher absorption of oxygen by the fatty acids than the oils can only be justified on the basis that the free carboxyl groups of the FFAs must have certain catalytic effect in the oxygen absorption process. In oils, the carboxyl groups are bound in form of ester linkage, and thus rendered unavailable for such catalytic effect. On the other hand, the presence of three-dimensional framework of the triglycerides (oils) provides suitable sites for the oxidative crosslinking reactions responsible for the drying/curing.

From the drying tests carried out, it was surprising to find that the oxygen absorption trend does not translate directly to the drying, though oxygen absorption is a primary stage subsequent to drying. Whereas the oils/drier mixtures dried between 3 to 4 h under testing parameter employed, the FFAs failed to pass the set-to-touch drying test. Even when the FFAs were incorporated with the curing agents at the given concentrations (10, 20, 30, 40, and 50 wt. %), the result on drying behaviour was still the same as in the case of pure FFAs. On the other hand, the curing agents obtained from a mixture of the pure oils and the driers underwent set-to-touch drying within the period 3 to 4 h on the average. These results show that FFAs not only lacked the geometry favourable for undergoing the drying process described but when present in oils can drastically hamper the drying rate of the latter. Consequently, it is strongly recommended that FFAs are reduced to the barest minimum possible in oils intended for paint formulation purposes in order to obtain paints with satisfactory drying rate to meet consumers' desire.

Conclusion

The oxygen absorption characteristics of oils of linseed, rubber seed and their corresponding fatty acids have been successfully carried out. The fatty acids display greater abilities in oxygen absorption than their oils. The results based on drying behaviours indicated that only the oils undergo drying by the method of set-to-touch but fatty acids did not. A different mechanism seems to underline the drying of oils, which is absent as in the autoxidation of fatty acids. The presence of FFAs was found to hamper the curing or drying of oils. Efforts must, therefore, be directed at minimizing the FFAs contents of drying oil mixtures, in consideration for paint formulation.

ACKNOWLEDGEMENTS

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