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# Efficiency of heavy metallic soap produced from naphthalic acid recovered from used lubricating oil in paint formulation

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#### **Abstract**

This work was carried out with the main aim of putting into use waste lubricating oil, thereby reducing the environmental hazard accruing to waste lubricating oil. This was achieved by the recovery of naphthenic acid from the used lubricating oil and consequently converting it to a heavy metallic soap drier (cobalt naphthenate) which was further used in an alkyd paint formulation. The cobalt naphthenate was produced by the double decomposition of cobalt chloride with sodium naphthenate. The sodium naphthenate was nevertheless first prepared from the reaction of sodium hydroxide and naphthenic acid extracted from the used/waste lubricating oil. The drying times of the formulated alkyd paint were then tested with respect to the mass of the drier added to a given quantity of the paint. The results were also compared with that of the commercial paint to ascertain its quality as regards to those sold in the market.

# 1. Introduction

Paints and coating occupy a prominent place in the cultural history of mankind. People have always been fascinated with colours and used paints to decorate and beautify themselves and their environment. The ancient paints consisted of animal fat and coloured earth or natural pigments such as ochre earth (Gorkum and Bouwman, 2005) thus they were based on the same principle as the paints that are used today a binder and a colouring agent. Alkyd resin are polyesters of poly functionical alchols and functionical carboxylic acids, where at least one component is at least trifunctional (Kalenda and Menc, 2009). The fundamental features of alkyd resin is a self reaction with oxygen from air ,resulting in the formation of a three dimensional polymer structure (Bieleman ,2002). Such paint materials thus form a solid film without addition of other component hardeners. The reactions between the oxidation drying paint and oxygen is known as autoxidation (Erich et al ,2006). The fundamental condition underlying autoxidation is presence of oxygen ,which diffuses through the paint film as well as the existence of a sufficient number of reactive sites inside the paint system . Such reactive sites are represented by double bonds introduced into the structure by the side chains of the unsaturated fatty acids (Kalenda and menc, 2009).the polymer network is formed via

hydroper0xides a relatively stable intermediate products of oxdiation (Erich etal, 2006). The decomposition to free radicals necessary for the subsequent reaction is very slow at room temperature, consequently drying of paint film is slow and the resulting hardness in adequate. Thus hydroperoxide decomposition can however be accelerated by means of suitable catalyst known as driers (Mallegol etal, 2001). As a result the drying time is completed within several hours. Driers generally are metal soaps or coordination compounds which accelerates paint drying. Thus shorteniing the total drying time of the paint (Bieleman, 2000).

The drying time of alkyd paint is essentially autoxidation process by transition metal salts(driers)(Gupta and Gauri,2013). And one very important type of this drier is the cobalt naphthenate, a transition metal salt obtained from a double decomposition of cobalt chloride and sodium naphthenate. The cobalt drier is a primary(active) type of drier which acts on the surface of the paint film(surface drier).

#### 2. Materials and Methods

Waste lubricating oil used was obtained from a mechanic workshop at Aroma, Awka, Anambra State. The oil was filtered to remove any solid contaminant.

# 2.1. Reagent Preparation

12% of NaOH was first prepared by weighing out 12 grammes of NaOH pellets into a measuring cylinder of 100ml. The sodium hydroxide pellets was first dissolved with little amount of distilled water. And then made up to 100ml.

# 2.2. Recovery of the Naphthenic Acid (as Sodium Naphthenate) from Used/ Waste Lubricating Oil

15ml of the filtered lube oil was collected and put into a beaker. 10ml of sodium hydroxide was added into the beaker containing the 15ml of filtered lube oil. The mixture was then heated at a temperature of  $110^{\rm O}$ C for 3 minutes and then left to cool. The aqueous layer of the mixture was separated using a syringe and then acidified with 6ml of conc.  $\rm H_2SO_4$ . An equal volume of 30ml of methanol and acetic acid were also added. The mixture was allowed to stand for 5 minutes to ensure proper settlling of the ppt formed. The aqueous part of the mixture was then decanted as sodium naphthenate into a separate clean beaker.

## 2.3. Preparation of Cobalt Naphthenate Drier

First 10% of cobalt chloride was prepared by weighing out 10 grammes of cobalt chloride into a measuring cylinder. The cobalt chloride was then dissolved with little amount of distilled water, before been made up to 100ml. The metallic soap (cobalt) drier was therefore produced by reacting appropriate quantity of the 10% cobalt chloride with the solution of the sodium naphthenate. The mixture was then heated for 5 minutes giving a purple coloured cobalt

naphthenate drier.

#### 2.4. Paint Formulation

Alkyd resin 30.00g
Titanium dioxide 20.00g
Antiskin 4 drops
Kerosene 50ml
Cobalt naphthenate Xg

# 2.5. Production of Alkyd Paint

The alkyd resin was put into a beaker and dissolved with kerosene. The kerosene was added little by little with constant stirring. The TiO<sub>2</sub> was also dissolved separately with a little amount of kerosene before been added into the alkyd resin while stirring. Other additives antiskin and the cobalt naphthenate drier were then added and stirred properly to homogeneity. Though a given quantity of the paint was measured out into different beakers before the different masses of the drier 1.0g, 1.5g and 2.0g were added into the paint and stored in a tight container.

# 2.6. Test on Drying Time of the Paint

The formulated paints were administered on a clean aluminum sheet with a brush. And the drying times of the paint as well as its film outlook were observed. The same was done to the commercial paint and the result of the drying times of the formulated paint and that of the commercial paint were taken and compared.

#### 2.7. The Soft-to-Touch Time Test (TSTT)

The paints were applied on a smooth aluminium sheet surface and monitored at room temperature. Lightly the films were touched with the tip of a clean finger, exerting enough pressure the finger was immediately placed against a clean sheet and was observed to be tacky as the film has not dried.

## 2.8. The Dry-to-Touch Time Test (TDTT)

The test films were lightly touched at intervals of time. And were assumed dry-to-touch when no considerable marks were left by the finger at approximately the same point on each observation.

## 2.9. The Dry-Hard Time Test (TDHT)

The films were touched with the tip of a clean finger exerting a considerable amount of pressure. The films were considered dry-hard when no noticeable change was observed on the films.

## 3. Results and Discussion

Results of the performance of the formulated paint is illustrated in Table 1, and compared with that of the commercial paint.

**Table 1.** Drying times of the formulated paint with respect to different masses of the cobalt naphthenate drier.

Type of Paint	Masses of Drier	Drying Times		
		TSTT	TDTT	TDHT
Formulate Paint	0.0g	60mins	7hrs	25hrs
Formulate Paint	1.0g	40min	5hrs	15hrs
,,,,	1.5g	28min	3hrs	12hrs
,,,,	2.0g	20mins	2hrs	8hrs
Commercial paint	Unknown	25mins	3hrs	10hrs

From the results in Table 1, it is infered that at 0.0g ie when no drier was added to the formulated paint, it took more time for the paints to dry, than when the drier is present. This proves the effectiveness of the drier as a dryaccelerating agent. Metallic soaps help in accelerating the rate of cross-linking of the double bonds in the unsaturated fatty acids and also increase flexibility of the paint molecules, increasing binding power and better adhesion of the paints on substrates (Nene, 2008). However when compared with that of the commercial paint, the formulated paint with a mass of 1.5g shows a very close drying time with that of the commercial paint than those of 1.0g and 2.0g driers. Although, the film surface of the formulated paint seemed to be rough (wrinkled) unlike the smooth film surface of the commercial paint. And this could be attributed to the use of an only one type of drier, active (cobalt) drier which is a primary drier that predominantly acts as a surface drier, where the dioxygen concentration is highest (Gorkum and Bouwman, 2005). Thus, as a result of the absence of a secondary drier which is supposed to dry the bulk of the film, the surface of the paint film wrinkles.

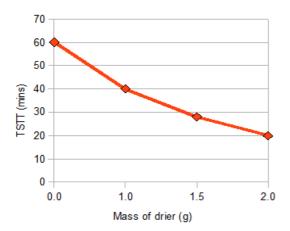


Fig. 1. The soft-to-touch time (TSTT)

The soft to touch time (TSTT) is a very important consideration in coating formulation, as coated surfaces may need to dry so that they can be put into service immediately after the coating has been supplied. The set – to–touch time as well as dry – through time of the paint samples depends on the amount of sunlight, volume of air and temperature of drying (Essien et al, 2012). From the result in Fig. 1, it is seen that as the mass of drier increases, the drying time decreases. It would be assumed that the increase in the mass of the drier increases the anions of the drier which is responsible for the faster drying properties of paint sample.

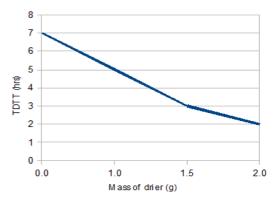


Fig. 2. The dry-to-touch time (TDTT)

The dry-to-touch time also followed the trend in The soft-to-touch-time. The more the mass of the drier, the less the time of drying. This could be attributed to the fact that driers belong to a class of soap which are added to both gloss, and water reducible alkyd paints to accelerate drying. They also increase drying process in other coating products like varnish. They are available as liquids, solids and pastes. It catalyzes the decomposition of peroxides and hydro peroxides formed by the action of atmospheric oxygen on binders like alkyd resins. This promotes the formation of radicals, and polymerization of the binder is thus initiated and accelerated (Ibanga, 2014).

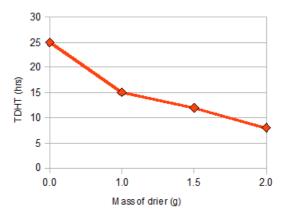


Fig. 3. The dry-hard-time (TDHT)

The results of the test analysed depict that the cobalt naphthenate drier has a positive effect on the formulated paint. Since, the formulated paint shows shorter drying time when the drier is present than when the drier is absent. Also from the graphical results, it was observed that the drying time of the paint film decreased with an increase in the amount of the drier used. Hence, driers has significant effect in paints (coatings) as it accelerates its drying rate. Although there is a wrinkling effect which could be attributed to the absence of a thorough drier (bulk drier) in the formulated paint. This then depicts the fact that cobalt is a primary drier, which only acts on the surface of the paint film leaving the bulk of the film. It could be concluded according to Nene (2008), that metallic soaps incorporated into a coating control the behavior of the color during its application or alter the properties of the finished product Nevertheless, care must be taken, while incorporating driers into a paint as only a little amount is needed to give a desired quality. Since excess of the drier can lead to paint failure.

#### 4. Conclusion

It is therefore, justifiable and recommendable that cobalt naphthenate can be produced from naphthenic acid recovered from used lubricating oil. This then serves as a means of recycling and reusing waste/used lubricating oil. Thereby ensuring waste management and economizing our resources. Also the cost of importing these driers from our foreign counterparts can be reduced by locally producing them. Government, industries and individuals should also ensure an effective way of collecting waste lubricating oil for recycling and reuse. To reduce the economic loss, environmental and health hazards accruing to poor waste lubricating oil disposal.

#### References

- [1] Andrews L. (2008), Compendium of recycling and destruction Technologies for waste oils "United Nations Environment Programme". Vol 2(4)pp 23-30
- [2] Anoliefo, GO and Vwioko D.E (2001), Tolerance of Chromolena edorata (L), K & R. Grown in soil contaminated with spent lubricating oil "Journal of Tropical Bioscience" Vol.1(1) pp 20-24.
- [3] Anwar N., Ali S.S., Anwar Z, Khattak J.Z, Jabbar A., Ansari T.M and Naqui S.R (2012), Recycling of Automotive lubricating waste oil and its Quality Assessment for Environment Friendly use "Research Journal of Environmental and Earth Sciences" Maxwell Scientific Organization Vol 4 (10) pp 912-916.
- [4] Bhaskar T., Uddin M. A, Muto. A., Sakata Y., Omura K., Kimura K. and Kawakami Y (2001), recycling of waste lubricant oil into chemical feedstock or fuel oil over supported iron oxide catalysts "Fuel" 83(1) pp 9-15.
- [5] Bieleman J. H. (2002), Driers "Chima" Vol.56 pp184-190.
- [6] Bieleman J.H (2000), Additives for coating, Wiley/VCH, Neinheim.
- [7] Bieleman J.H (2002), Progress in the development of cobalt free drier systems "Macromol Symp" Vol. 187, pp 811-821.
- [8] Cotton, F.O. (1982). Waste Lubricating Oil, An Annotated Review (REVISION DEB3001439 of Annotated Review 1997), BETC/IC 7914) CORP SOURCE – Department of Energy, Bartles Ville.
- [9] Denton J.E (2007), A review of the potential human and Environmental health Impacts of Synthetic motor oils, "Office of Environmental health Hazard Assessment California Environmental Protection Agency" April.
- [10] Emengo F.N, Orakwue F.C. and Ajiwe V.I.E (2001), Extraction of Naphthenic acids from waste lubricating oil, conversion to heavy metallic soaps and subsequent paint formulations "African Journal of Science" Vol.2, pp 323-330.
- [11] Erich S.J.F, Laven J. Pel. L., Huinik H.P and Kopinga K (2006), Influence of Catalyst type of the curing process and

- network with different catalysts "Progress in Organic Coatings" Vol. 55, pp 105-111.
- [12] Essien E. A., Umoren S.A, Essien E.E, Udoh A.P (2012) Preparation and Evaluation of Cucumeropsis mannii Naud. Seed Oil Metallic Soaps as Driers in Gloss Paint. J. Mater. Environ. Sci. 3 (3) (2012) 477-484
- [13] Frankel E.N (1998), Lipid Oxidation. The oily press Ltd. Dundee.
- [14] Gorkum R. and Bouwman E. (2005), The Oxidative drying of alkyd paint catalysed by metal complexes "Coordination Chemistry Reviews" Vol.249, pp 1709-1728.
- [15] Gupta A and Gauri S.K (2013), Determination of optimal quantities of different types of driers for addition in the batches of paint formulation "International Journal of Engineering, Science and Technology" Vol.5, No.4, pp 1-13 India Statistical Institute, Kolkata.
- [16] Hsu Y.L, Lee C. H and Kreng V.B (2011), Analysis and Comparison of Regenerative Technologies of waste "Transactions on Environment and Development" Vol.5(3) pp 295-309.
- [17] Ibanga O. I. (2014) Extraction, Characterization of African Pear (Dacryodes Edulis) Oil and its Application in Synthesis and Evaluation of Surface Coating Driers. International Journal of Advanced Research in Chemical Science (IJARCS) 1(4), 14-22.
- [18] 1Jha M.K (2005), Re-refining of used lube oils "An intelligent and eco-friendly option "Indian Chemical Engineering" 47(3) pp 209-211.
- [19] Joana V. and Barbosa F. (2013), Development of monomers for production of high performance paints "Department of Chemical Engineering University of Porto" pp 15-23.
- [20] Kalenda P and Menc p. (2009), Contribution of Inorganic pigments to the formation of paint films "Transfer Inovacii" Czech Republic pp 6-8.
- [21] Kalichersky V.A and Peter E,H (1960), Petroleum, our man of all work: The raw materials crude petroleum. Mc Graw Hill. New York P22.
- [22] Kayode J, Oyedeji A.A, and Olowoye O.S (2009), Evaluation of the effects of pollution with spent lubricating oil on the physical and chemical properties of the soil "The pacific Journal of Science and Technology "Vol. 10, No.1, May pp 387-391.
- [23] Kinghorn R.R.F, 1983, An introduction to the physics and Chemistry of Petroleum, Wiley and Sons, New York.
- [24] Mallegol J., Lemaire J., Gardette J. (2000) Drier Influence on the curing on linseed oil, "Progress In Organic Coatings" Vol.39, pp 107-113.
- [25] Mallegol J; Gonon L., Commereuc S. and Verney V. (2001), Thermal (DSC) and Chemical iodometric titration/methods of Peroxide Measurements in order to monitor drying extent of alkyd resins "Progress in Organic Coatings" Vol.41, pp 171-176.
- [26] Micciche F. Oostreen E. Van Haveren J. and Van der Linde R (2005), The combination of reducing agents/iron as environmentally friendlier alternatives for co-based driers in the drying of alkyd paints "Progress in Organic Coatings" Vol.53, pp 99-105.

- [27] Motshumi J.D, Muzenda E.,Pilusa T.P, and Mollagee M. (2013) "2ND International Conference on Environment, Agriculture and Food Sciences" August 25-26, Kuala Lumpur. Pp106-109
- [28] Nene P. N. (2008) Studies on the Suitability of Metallic Soaps and Kaolin (White Dirt) in the Formulation of Pigment Coating for Paper. Advances in Natural and Applied Sciences, 2(2): 73-76.
- [29] Nowak M. (2006), Driers "Coatings Technology Handbook" 3<sup>rd</sup> Ed pg 80-83.
- [30] Othmer K. (1967) Encyclopedia of Chemical Technology, 2<sup>nd</sup> Ed. Vol. 13. John Wiley and Sons inc New York p727.
- [31] Oyman Z. O, Ming W, Van der Linde K. (2003), Oxidation of model Compound Emulsions for alkyd paints under the influence of cobalt drier "progress in Organic Coatings" Vol.48, pp 80-91.
- [32] Plain Language Guide (2013) used oil and waste fuel

- management Regulations, "Environment and Natural Resources Northwest Territories, December.
- [33] Ploeger R and Chiantore O (2012), Characterization and Stability Issues of Artists' Alkyd Paints "Department of Chemistry University of Torino via Pietro Giuria" Torino pp 23-30.
- [34] Sharma B.K (2011), Industrial Chemistry Including Chemical Engineering, 16<sup>th</sup> Ed Krishna Parashan Media Ltd., Meerat pp246-256.
- [35] U.S. High Production Volume (HPV) Chemical Challenge Program (2005), Summary of existing data proposed test plan and rationale for cobalt naphthenate, prepared by morning star consulting Inc. December 23.
- [36] Vazquez Duhalt R. (1989), Environmental Impact of used motor oil "Science Total Environment" 79(1) pp 1-23.
- [37] www.lookchem.com (september 2013)