A Comparison of Cardanol and its Derivatives as Reactive Diluents in Alkyd Coatings

Njuku, F.W[.1*], Mwangi, P.M[1] and Thiong'o, G. T[1]
[1]Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology,
P.O. Box 62,000-00200, Nairobi, Kenya.
Telephone +254-713559697.
* E-mail of the corresponding author: njukufrancis@ymail.com

Abstract

Volatile Organic Compounds (VOC's) have aroused concern in many parts of the world especially in large cities due to their negative impact to the environment. In the presence of sunlight, VOC react with NOx gases to produce tropospheric ozone, a powerful oxidant and pollutant to the atmosphere. Although most of the VOC's originate from petroleum products and internal engine exhausts, and plants, a significant amount is derived from solvent based coatings. Cardanyl methyl ether, cardanol acetate synthesized from cardanol and neat cardanol, which was isolated from cashew nut shell liquid, recovered from cashew nut shell and neat cardanol were studied for their characteristics and evaluated for their suitability as reactive diluents in alkyd coatings. These products were found to be compatible with long alkyd coatings. The reactive diluents helped to lower volatile organic compounds (VOC), drying time and application viscosity of alkyd based coatings. Coatings formed had excellent adhesion, better drying time, and pencil hardness and are cheaper since CNSL is a renewable raw material. VOC reduction to the extent of about 39 % compared to conventional commercial products was realized. Use of the reactive diluents developed would not only reduce direct pollution through VOC's from coatings, but also pollution generated from burning cashew nut shells, which is currently widely practiced among cashew nut processors.

Keywords: Cardanyl methyl ether, Cardanol acetate, cardanol, reactive diluent, Alkyd Coatings

1.0 Introduction

Environmental concern has become one of the most important topics in the coatings industry which has led researchers to continually attempt to develop coatings system with less solvent. VOCs are regulated because of their potential to generate ozone when emitted in polluted urban environments (Daniel and Scott, 2004). For this reason, a suitable reactive diluent for air-drying alkyd paints should be developed with suitable reactive sites for efficient oxidative curing. The functional groups within the reactive diluent have major effects on its reactivity. In addition, successful reactive diluents should maintain low viscosity. Cashew Nut Shell Liquid (CNSL) is an agricultural renewable resource and a by-product of the cashew industry (Risfaheria *et al*., 2009). It is the source of saturated and unsaturated hydrocarbon phenols, an excellent monomer for thermosetting polymers production and therefore holds a considerable promise in the different applications such as in the coating industry. Vacuum distillation of raw CNSL or chemical isolation yields pure cardanol. Cardanol is n-pentadecadienylphenol; the aliphatic side chain usually consists of mixture of one, two and three double bonds in a linear chain together with a saturated side chain. CNSL and cardanol are used in the manufacture of special phenol resins for coatings, lamination and as friction materials. These polymers are synthesized from CNSL or cardanol either by polycondensation with electrophylic compounds such as formaldehyde, furfuraldehyde or by chain polymerization through unsaturation presented in the side chain using an acid and base catalyst (Ranjana *et al*., 2008). Alkyd resins are polyesters produced by condensation polymerization of three types of monomers that is polyols, polybasic acids and fatty acids or triacylglycerol (Ursula *et al.*, 2010). Characterization included Gas-chromatography Mass spectrometer (GC-MS) and Fourier transform infra-red spectroscopy (FTIR).The resulting reactive diluent was evaluated in long oil alkyds. Formulations included incorporation into the resin of reactive diluents as a substitute for some of the solvent, metal driers. Coatings formed were studied to determine the influence of reactive diluent on the alkyd resin system in terms of viscosity, dry time, and film properties. Properties were compared to those of controls formulated alkyd resin without reactive diluent. In this study, we looked at the effect of Cardanol acetate, cardanyl methyl ether and neat cardanol as partial replacements for mineral spirits in long oil alkyds. Due to the high presence of double bonds in cardanol acetate, cardanyl methyl ether and neat cardanol, we expected an improvement in drying time and hardness development.

2.0 Material and Methods

2.1 Analytical Equipment

Analytical GC-MS was performed on a Finnigan GC 8000 series with a voyager EI- mass selective detector and a RTX-5MS column. FTIR spectra were recorded using a Shimadzu model 8400 spectrometer on KBr plates. The viscosity was measured using a capillary viscometer number 3 viscometer (Kusako Scientific Instrument, Japan) and NDJ-5S digital viscometer at 60 rpm. The drying time was measured using a Quadracycle electronic drying time recorder DT 5040 from Gardco Company of USA.

2.2 General

Raw CNSL was obtained by extraction of ground shells of cashew nut by batch simulation of counter current method using n-hexane. Cardanol was isolated from decarboxylated CNSL using methanol and ammonia solution and purified to obtain pure product. Methyl Iodide was obtained from the Lobachemie PVT limited Mumbai, India and acetic anhydride from Sigma Aldrich Laborchemikalien, Germany. Wijs solution (Sigma-Aldrich) and n-Hexane (Sigma-Aldrich) were used without further purification. Long oil alkyd resins (70 %) and metal driers (32 % Lead Naphthenate and 10 % cobalt octoate) were used for formulation with reactive diluents.

2.3 Synthesis of Cardanol Acetate

The method described by Saeid and Somayeh, 2010 was adopted. Cardanol (31.6 g), acetic anhydride (15.8 g), concentrated sulphuric acid (0.4 g) and acetonitrile (10 ml) mixed together. The reaction mixture was refluxed at 80 ^{o}C in a water bath for 4.5 hrs. After completion of the reaction, the mixture was filtered off. The product was extracted with ethyl acetate and washed with water and finally dried over anhydrous sodium sulphate to obtain pure product

2.4 Synthesis of Cardanyl Methyl Ether

Cardanol (23.5 g), methyl iodide (30.3 g), anhydrous potassium carbonates (34.6 g) and 100 ml of acetone were mixed together. The mixture was refluxed on a hot plate for 8 hours. After completion of the reaction, the mixture was poured into 500 ml of water in a beaker. The organic layer was separated and extracted with (3 × 20 ml) diethyl ether. The combined organic layer and diethyl ether extract was washed with 2 M sodium hydroxide solution and dried over anhydrous sodium sulphate. The diethyl ether was removed in a rotary evaporator under reduced pressure to obtain pure product (Brian, 1989).

2.5 Alkyds' Formulation

The alkyds resin was diluted with reactive diluent at weight percentages of 5 %, 10 %, 15 % 20 %, and 25 %. Metal driers were added at levels 1.0 % and 0.6 % for lead naphthenate and cobalt octoate respectively. A typical commercial coating was also used as a standard.

2.6 Tests for Volatile Organic Compounds

Testing of volatile organic compounds was done in a dry oven model advantec KL-420 electric muffle furnace from Toyo Seisakusho Company limited. It was operated by adopting the ASTM D 2369 (5). The oven was preheated to 100 + 5 °C for approximately 30 min. A crucible was weighed using a Denver instrument XL-1810 scale. This weight was recorded. While the crucible was still on the scale, the scale was tared and approximately 1 g of the sample swirled onto the crucible. After the samples had been prepared, they were placed into the preheated oven for 60 min. At the conclusion of 60 min, the samples were immediately removed from the oven and weighed. The percent volatile was calculated according to the formula below. An average value of the samples was taken as the result for the samples.

$$\text{Volatile content, } (\%) = \frac{w2 - w3}{w2 - w1} \times 100$$

Where, w_1 = weight of crucible, g
w_2 = weight of crucible + sample, g
w_3 = weight of crucible + sample, after heating, g

2.7 Viscosity Test for the Formulations

The viscosity was measured by NDJ-5S digital viscosity viscometer at room temperature (23 ^{o}C). Rotor number one was used at 60 rotations per minute rotating speed (shear rate of 100 mPa.s). Approximately 100-200 g of samples was prepared in a 200 ml beaker and mixed on roll mill for 30 min.

2.8 Tests for Adhesion of Coating Film to the Metal Surface

Adhesion test study was evaluated by adopting ASTM standard (D 3359-09e2) method. Cross-cut tape test was undertaken to assess the adhesion of coatings on the metal panel. After curing the coating by air-drying for 10 days, panel were held firmly and then six cross-cuts, 1 mm apart, were made manually on the coated surface. The detached flakes or ribbons of coating were removed from the surface with a soft brush. A strip of fiber-reinforced cellulose acetate pressure-sensitive tape was then placed over the surface of the metal panel. The tape was manually smoothed, and pressure was applied using a rubber eraser to ensure good contact between the tape and the coating film. After 1 minute of application, the tape was removed from the coated surface by rapidly pulling it off, back upon itself, at an angle as close to 180° as possible. The grid area was inspected for removal of coating from the panel surface using an illuminated magnifier. The rate of adhesion was averaged for six panels of each group based on the code given in the standard for classification.

2.9 Tests for Drying Time

Drying time study was evaluated by adopting ASTM standard (D 5895-03) method using a Quadracycle electronic drying time recorder DT 5040 as shown in Plate 1. The coating (2 mils wet thickness) was applied to a glass panel using a Bird Film Applicator (from Gardco Company) and a circular dry time recorder was immediately placed on the wet film. The drying time was observed.

Plate 1: Drying time test of coating on a glass panel using a Quadracycle electronic drying time recorder DT 5040

3.0 Tests for Pencil Hardness

This test was carried out by adopting the ASTM D 3363 method using a HA-3401 Gardco/Wolff Wilborn mechanical pencil scratch hardness kit. Pencils of increasing hardness values were moved over the substrate surface in a precisely defined way using a mechanical pencil lead holder by applying sufficient pressure so that the coating film was damaged by the lead or the pencil point were crushed. Surface hardness was defined by the hardest pencil grade which failed to damage the surface

4.0 Results and Discussion

4.1 Characteristics of neat cardanol, cardanol acetate and cardanyl methyl ether

Table 1 presents physical characteristics of alkyd coating formulations with neat cardanol, cardanol acetate and cardanyl methyl ether as reactive diluents. There is a significance difference in the viscosity values of neat cardanol, cardanol acetate and cardanyl methyl ether. Cardanyl methyl ether had a low viscosity as compared to neat cardanol and cardanol acetate because of the architecture of the molecule, the substituents in the phenyl core orient themselves in such a way that the molecules do not interact as they flow down the capillary tube. There is reduced shear rate and as a result the shear strain increases and the molecules flow easily as compared to cardanol acetate. In neat cardanol, there is molecular interaction (hydrogen bonding) which results into the entanglement of the long aliphatic chain and the viscosity is increased. There is no significance difference in the iodine values of neat cardanol, cardanol acetate and cardanyl methyl ether (Table 1). This shows that methylation and acetylation of cardanol with methyl Iodide and acetic anhydride respectively does not affect the unsaturation of the side chain. There is a significance difference in the density values of cardanyl methyl ether and cardanol acetate. This is because acetylation increases the molecular weight of the phenyl backbone. There is no significance difference in the moisture content of cardanol ether and cardanol acetate as shown in the Table 1

Table 1: Comparison of the characteristics of Cardanyl methyl ether, cardanol acetate and neat cardanol

Parameter	**Cardanyl methyl ether**	**Cardanol acetate**	**Cardanol**
Specific gravity at 25 ^{o}C, g/cm^{3}	0.93	0.96	0.93
Viscosity at 40 ^{o}C, mPa.s	36.10	42.06	45.31
Iodine value, g/100 g	232.6	232.4	232.0
Moisture content (%)	Negligible	Negligible	Negligible
pH @25 ^{o}C	7.01	6.23	6.16

4.2 Identification of cardanol, cardanol acetate and cardanyl methyl ether using the FTIR

Figures 1, 2 and 3 represents FTIR spectra of neat cardanol, cardanol acetate and cardanyl methyl ether respectively. In Figure 2, absorption peak at 3350.1 cm $^{-1}$ indicated the presence of O-H stretch for phenolic compounds. The peaks that appeared at frequency of 3008.7 cm^{-1} indicated the presence of C-H symmetrical stretch of the aromatic compounds (Figure 1, 2 and 3). The peak that appeared at frequency 2925.8 cm-^{1} indicated the presence of methylene C-H symmetrical stretch of the long aliphatic chain (Figure1, 2 and 3). The Spectra that appeared at 1265.2 cm^{-1} area indicated C-O symmetrical stretch of the phenolic compounds (Figure 2). The absorption peak that appeared at the 1596.9 cm^{-1}, 1587.3 cm^{-1} frequency indicated C=C stretch of the long aliphatic chain (Figure 1 and 2) respectively, while the peak that appeared in the 1458.1 cm^{-1} frequency indicated the C=C symmetrical stretch of the aromatic chains. The peak that appeared at frequency 1770.5 cm-^{1} indicated the presence of C=O stretch for an ester (Figure 2). The peak that appeared at 1205.4 cm^{-1} indicated C-O symmetrical stretch characteristic of an ester (Figure 2). The peak that appeared at frequency 1768.6 cm-^{1} indicated the presence of C=O stretch for an ester. The peak that appeared at 1205.4 cm^{-1} indicated C-O symmetrical stretch characteristic of an ether (Figure 3).

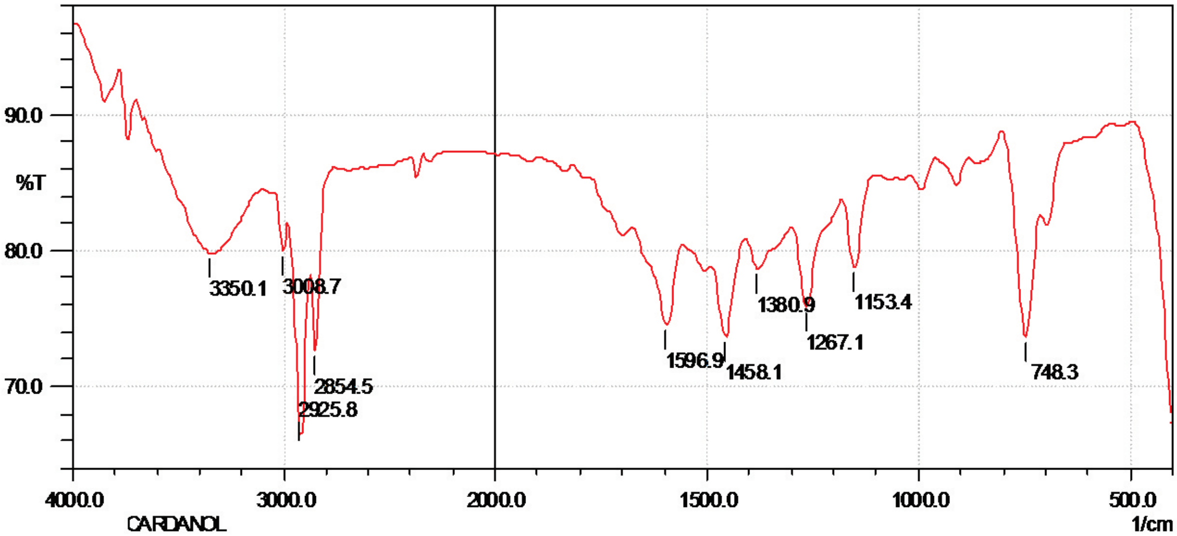

Figure 1: FTIR Spectrum of cardanol

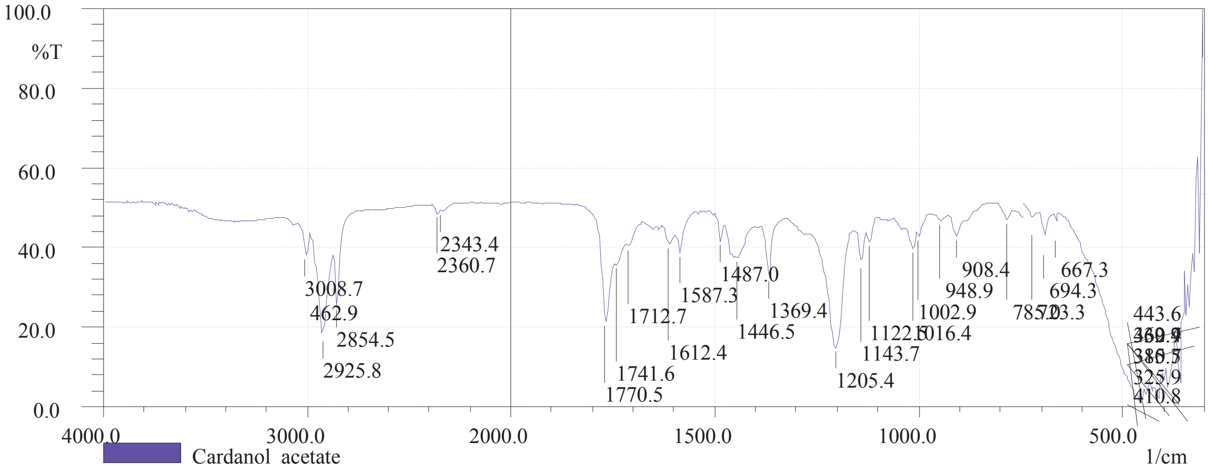

Figure 2: FTIR spectrum of cardanol acetate

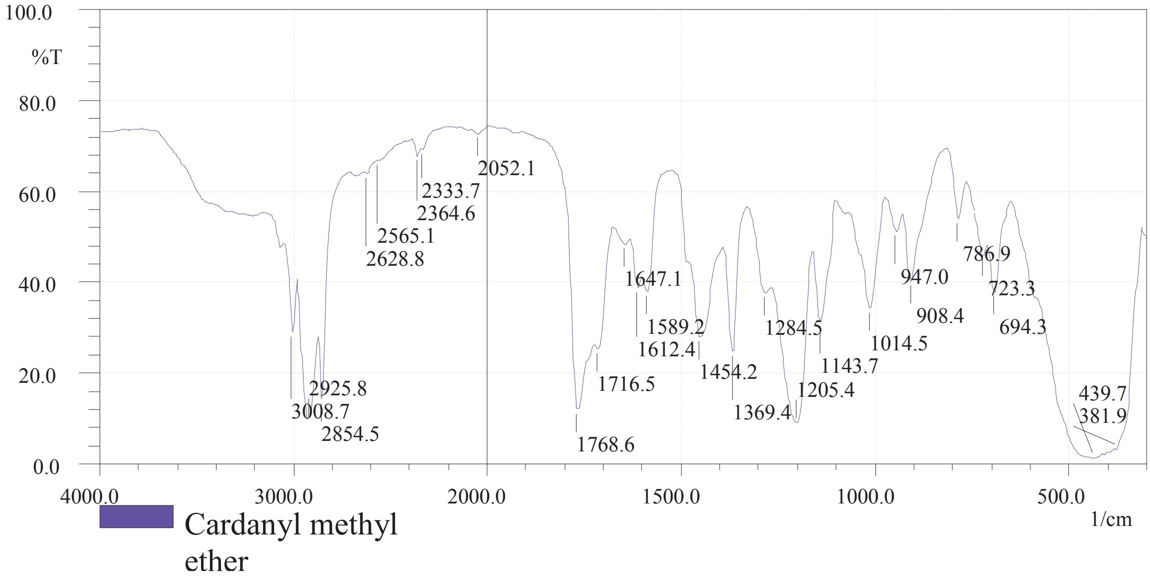

Figure 3: FTIR spectrum of cardanyl methyl ether

4.3 Interpretation of GC MS profile for neat cardanol, cardanol acetate and cardanyl methyl ether

Figures 4, 5 and 6 represent GC-MS profiles for neat cardanol, cardanol acetate and cardanyl methyl ether respectively. The base peak at m/z = 108 for cardanol, cardanol acetate and cardanyl methyl ether of the spectra's can be rationalized in accordance with the main characteristic of alkyl benzene as derived from the molecular ions and is attributed through the β cleavage of the aliphatic chain as shown in all the three figures. There is Mclaffetry rearrangement due to the long aliphatic chain attached to the benzyl ring (Fred and Frantisek, 1993). The Peak at m/z = 302 and 304 correspond to the molecular weights of the two fractions of cardanol as shown in Figure 4. The Peak at m/z = 340, 344 and 346 correspond to the molecular ions of the three fractions of cardanol acetate (Figure 5).

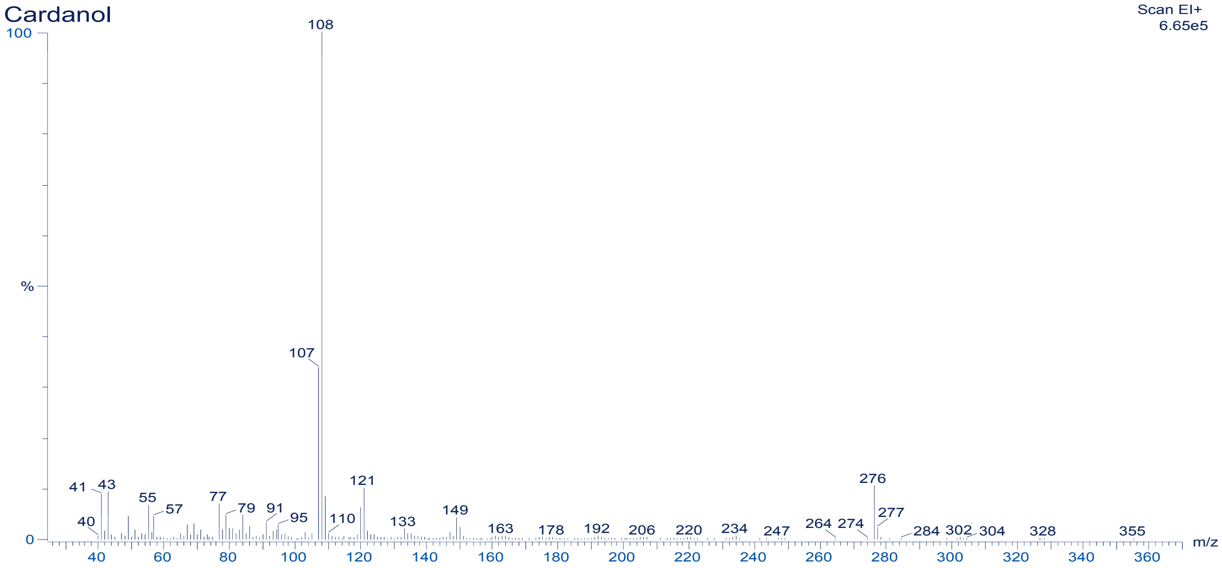

Figure 4: GC MS profile of cardanol

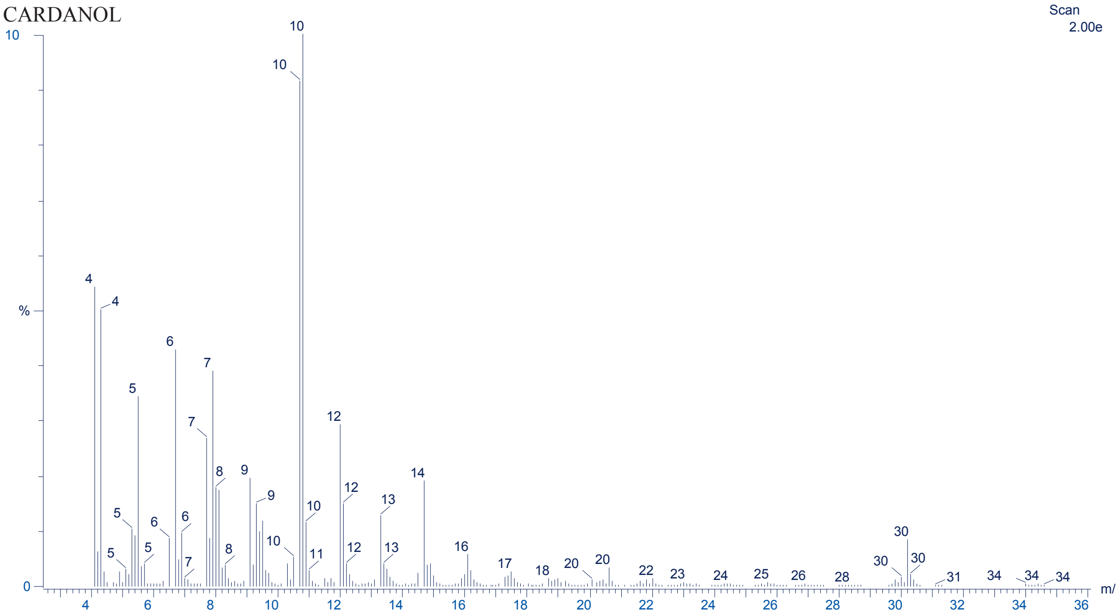

Figure 5: GC MS profile of cardanol acetate

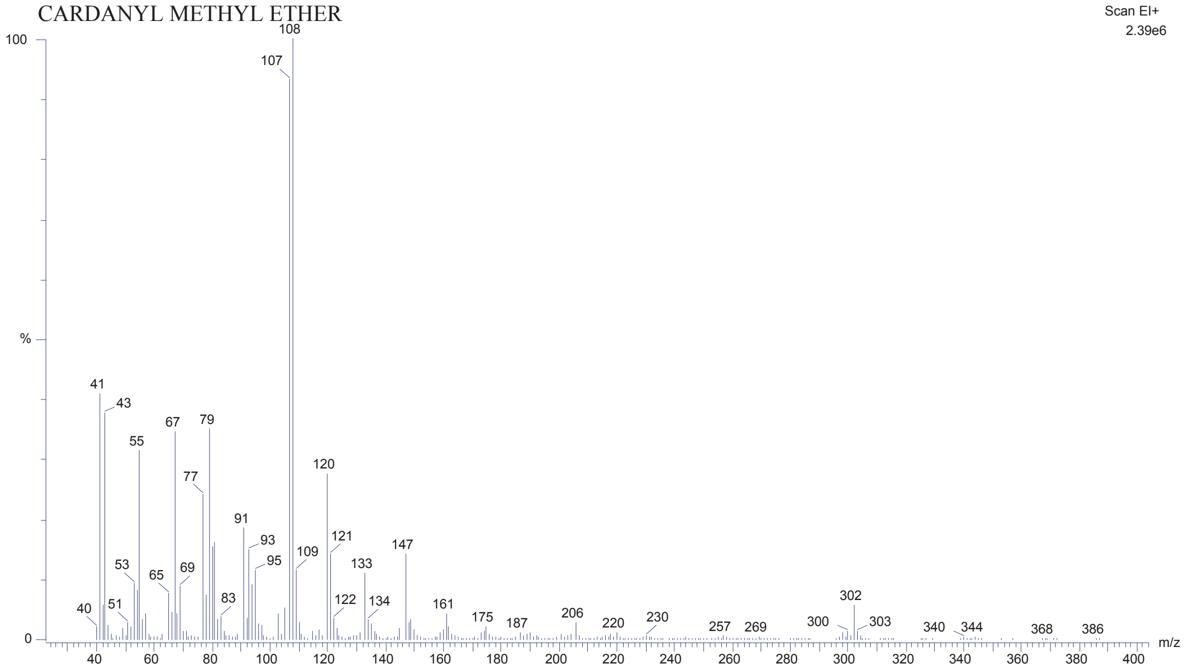

Figure 6: GC MS profile for cardanyl methyl ether

4.4 Viscosity of the coating formulations

The viscosity reducing abilities of cardanyl methyl ether, cardanol acetate and neat cardanol were tested at different weight percentages in alkyd coatings. It was found that cardanyl methyl ether had an inherently lower viscosity than cardanol acetate and neat cardanol (Figure 7). Cardanyl methyl ether has a lower molecular weight compared to Cardanol acetate, which has a higher molecular weight due to the acetate group. Cardanyl methyl ether, cardanol acetate and neat cardanol all showed good compatibility with alkyd resin; however, Cardanyl methyl ether exhibited a much better viscosity reducing ability than cardanol acetate and neat cardanol. Only 20 wt% of cardanyl methyl ether reduced the alkyd resin viscosity to value below 500 mPa·s, which is required for many applications. At least 15 wt % of cardanol acetate was needed to reduce alkyd resin to the same viscosity.

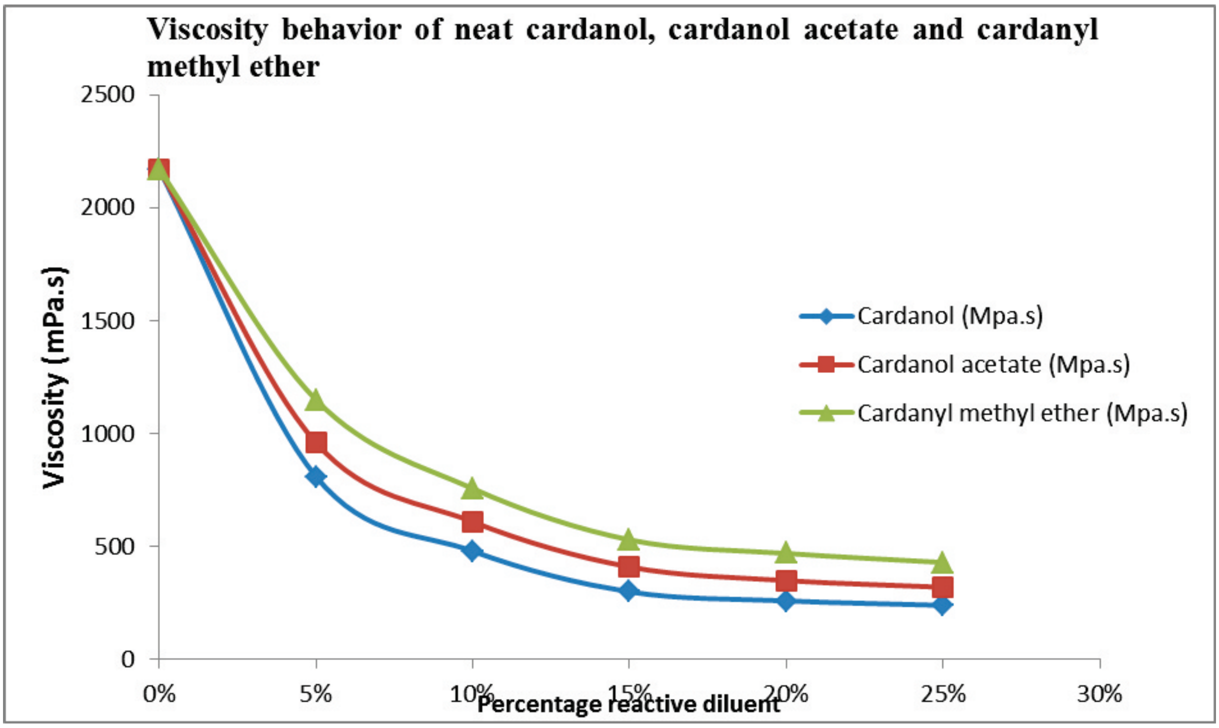

Figure 7: Viscosity levels of neat cardanol, cardanol acetate and cardanyl methyl ether

4.5 Drying performance of reactive diluent–alkyd formulations

Drying times increased with increasing reactive diluent concentration as presented in Table 2. The amount of diluent added into the system affected the drying mechanism to be slower. Drying times of alkyd coatings with neat cardanol, cardanol acetate and cardanyl methyl ether were between 7 and 8 hours. However, cardanyl methyl ether diluent had improved drying time from 7 h at 20 weight percent added to alkyd system. At 20 wt% of cardanyl methyl ether modified diluent, dry time of the system was different as compared to neat cardanol and cardanol acetate, the dry time was reduced with the amount of cardanyl methyl ether modified diluent. It was noted that dry time of alkyd system was improved greatly by cardanyl methyl ether modified diluent as compared to neat cardanol and cardanol acetate. Dry time of cardanyl methyl ether modified diluent with alkyd systems were around 7 h comparing to 6 h of the control. The improvement of drying time by cardanyl methyl ether modified diluent could be explained by the higher functionality due to the double bonds and low viscosity of the system. Low viscosity provided mobility to the long aliphatic chain to react; therefore, the curing time was faster.

Table 2: Drying times of alkyd coating formulations blended with reactive diluents

	Alkyd/neat cardanol (h)	**Alkyd/cardanol acetate (h)**	**Alkyd/ cardanyl methyl ether (h)**
Control weight (%)	6	6	6
5	7	7	7
10	7	7	7
15	7	7	7
20	8	8	7
25	8	8	8

4.6 Pencil Hardness and adhesion for neat cardanol, cardanol acetate and cardanyl methyl ether –alkyd films

Pencil hardness and adhesion results for neat cardanol, cardanol acetate and cardanyl methyl ether are presented in Table 3 and Table 4 respectively. The pencil hardness of the films also improved as predicted for the reactive diluents and remained the same for systems containing neat cardanol, cardanol acetate and cardanyl methyl ether. Addition of reactive diluents with the metal driers resulted in films with good pencil hardness compared to the controls. All films were relatively hard, based on the pencil hardness tests, and all films displayed constant hardness with reactive diluent. All these reactive diluents had good pencil hardness because they contain a rigid aromatic structure. Adhesion was good in both reactive diluent and control films, and this could be attributed to the double bonds that form strong polymer networks in the coating. Crosslink density versus time, is improved in all reactive diluent–alkyd mixtures relative to controls. These results validate that the reactive diluent plays a role in increasing chemical cross-linking between alkyds and is incorporated throughout the polymer network of the dried alkyd films.

Table 3: Result for pencil hardness test on coatings based on alkyd resin: i) with neat cardanol, ii) with cardanol acetate and iii) with cardanyl methyl ether mixture (after 10 days of curing)

Percentage reactive (%)	**Cardanol**	**Cardanol acetate**	**Cardanyl methyl ether**
0 %	5H	5H	5H
5 %	4H	4H	4H
10 %	4H	4H	4H
15 %	4H	4H	4H
20 %	4H	4H	4H
25 %	4H	4H	4H

Table 4: Adhesion test on alkyd resin with i) neat cardanol, ii) with cardanol acetate and iii) with cardanyl methyl ether (after 10 days)

Percentage reactive (%)	**Cardanol**	**Cardanol acetate**	**Cardanyl methyl ether**
0 %	5B	5B	5B
5 %	5B	5B	5B
10 %	4B	4B	4B
15 %	4B	4B	4B
20 %	4B	4B	4B
25 %	4B	4B	4B

4.7 Volatile organic content

The calculated VOC content of all the formulation studied are presented in Tables 5. Neat cardanol, cardanol acetate and cardanyl methyl ether reduce VOC when used as reactive diluents. The study indicates that it is possible to formulate compositions having substantially lower VOC and higher solids due to lower viscosities of neat cardanol, cardanol acetate and cardanyl methyl ether compared to commercially prepared formulations.

Cardanol acetate, Cardanyl methyl ether and neat cardanol had good solubility and compatibility with alkyd resin resulting in very low Volatile Organic coating formulations.

Table 5: Result for Volatile Organic Compounds on alkyd resin– neat cardanol mixture, alkyd resin– cardanol acetate mixture and alkyd resin– cardanyl methyl ether mixture (after 10 days)

Percentage reactive diluent	**VOC (% wt) Neat cardanol**	**VOC (% wt) Cardanol acetate**	**VOC (% wt) Cardanyl methyl ether**
0 %	47.24	47.17	47.21
5 %	45.90	45.81	46.51
10 %	44.59	44.63	44.71
15 %	43.72	43.83	43.79
20 %	41.20	41.31	41.41
25 %	39.23	39.28	39.31

5.0 Conclusions

Coating formed with Cardanyl methyl ether systems had significantly reduced viscosity compared to Cardanol acetate and neat cardanol. Cardanol acetate, Cardanyl methyl ether and neat cardanol displayed improved adhesion and pencil hardness, a reduction in volatile organic content in addition to an inherently low viscosity and efficient viscosity reduction and should therefore be more attractive as reactive diluents.

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References

1. Alp, H. A., Kevin, D., Rhonda, R., Crystal, S., James, W. R. and Sarah, E. M.(2011). Synthesis and evaluation of tetra (2, 7-octadienyl) titanate as a reactive diluent for air-drying alkyd paints. *Journal of coatings technology and Research*, **8** (1): pp 45–52.
2. ASTM standard D 3363-05, 2011e2, “Standard Test Method for Film Hardness by Pencil Test,”ASTM International, New York, PA, 2011,10.1520/ NY 10036,www.astm.org
3. ASTM standard D 3359-09e2, “Standard Test Method for Measuring Adhesion by Tape Test,” ASTM International, New York, PA, 2009,10.1520/ NY 10036, www.astm.org
4. ASTM standard D 5895-03, 2008, “Standard Test Method for Evaluating Drying or Curing During Film Formation of Organic Coatings using Mechanical Recorders,”ASTM International, New York, PA, 2008,10.1520/ NY 10036, www.astm.org
5. Atul, M., Sudhir, J and Powar, A. G. (2011). Cashew nut processing: Sources of environmental pollution and standards. *Indian Journal*, 1: pp 05-11Ranjana, Y. and Deepak, S.(2008). Studies of cardanol based epoxidizednovalac resin and its blends. *Indian journal of Chemistry and Chemical technology*, **2**: pp 173-184.
6. Brian, S. F., Antony, J. H., Peter, W. G .S. and Austin, R. T.(1989). Vogels text book of practical organic chemistry, 5thed, pp 986. John wiley and sons, New york
7. Bambang, Susilo.(2000). Roasting experiment of cashew nut in traditional industry. *Journal of Agricultural and Technology,* **1**: pp 64-69.
8. Barrett, K. E. J. and Lambourne, R.(1966). Air-drying alkyd paints. The effect of incorporation of non-volatile monomers on film properties. *Journal of the Oil and Colour Chemists Association,* **49**(6): pp 443-63.
9. Cornelius, J. A. (1966). Cashew nut shell liquid and related materials. *Tropical science*, **8**: pp 79-84.
10. Daniel, B. P and Scott, E. S. (2004). High-Solids Alkyd Resins with Improved Properties Based on Styrene Allyl Alcohol Resinous polyols. *Journal of Coatings technology*, **1**: pp 40-47.
11. De Lima, S. G., Feitosa, C. M., Cito, A. M. G. L., Neto, M. J. M.,Lopes, J. A. D., Leite, A. S., Brito, M. C., Dantas, S. M. M. andMeloCavalcante, A. A. C.(2008). Effects of immature cashew nut shell liquid

(*Anacardiumoccidentale*) against oxidative damage in *Saccharomyces cerevisiae*and inhibition of acetylcholinesterase activity. *Journal of Genetics and Molecular Research,* **7** (3): pp 806-818.

12. Dieter, S and Werner, F**.** (1998). Paints, Coatings and Solvents. Book, 2nd edition, pp 41-50, New York: Wiley-Vs.
13. Francisco, H. A. R., Judith P. A. F., Nagila, M. P. S. R., Francisco C. F. de Franca., Jose O. B. C. (2006). Antioxidant activity of cashew nut shell liquid (CNSL) derivatives on the thermal oxidation of synthetic *cis*-1, 4-polyisoprene. *Journal of Brazilian Chemical Society*, **17:**pp1.
14. Fred W. M and Frantisek, T (1993). Interpretation of Mass Spectra: Mass spectra of common Compound Classes. 3 rd edition,pp 226-260, John Wiley and sons
15. Hatsuo, I and Tarek, A.(2011). Handbook of Benzoxazine Resins: Study of a cardanol-Based Benzoxazine as Reactive Diluent and Toughening Agent of Conventional Benzoxazines. pp 365, Elsevier B.V.
16. Hochberg, S. (1965). Thechemistry of the vinyl cyclic acetals and their air-drying reactions*. Journal of the Oil and Colour Chemists Association*, **48**: pp 1043-1064.
17. James, J. L**.** (2003).Coating materials for electronic applications: *Polymer processes, reliability, testing*.2ed: pp 71-73.Voges publication/William Andrew (USA).
18. Johansson, K and Johansson, M.(2006). Progress in organic coatings: *A model study on fatty acid methyl esters as reactive diluents in thermally cured coil coating systems*. **55:** pp 382-387.
19. Knop, A. and Scheib, W. (1979). Chemistry and Applications of Phenolic Resin-Polymer Properties and Applications; 2ed, Springer Verlag: Berlin, Germany.
20. Khumar. P. P., Paramashivappa, P. J., Vithayatil, P. V. S. R, and Rao, A. S**.** (2002). Process for isolation of cardanol from technical cashew (*Anacardiumoccidentale*) nut shell liquid. *Journal of Agriculture and Food Chemistry*, **50**: pp 4705-4708.
21. Larson, D. B. and Emmons, W. D**.** (1983). Chemistry of high-solids alkyd/reactive diluent coatings*. Journal of Coatings Technology*, **55**(702): pp 49-56.
22. Mahanwar, P. A. and Kale, D. D.(1996).Effect of cashew nut shell liquid (CNSL) on properties of phenolic resins. *Journal of Applied Polymer Sciences*, **61**: pp 2107-2111.
23. Marcionilia, F. P., Denis, D. L., Leonardo R. M., Adilson B., Sandra, T. S., Leticia, V. C. L**.** (2009). Ecotoxicological analysis of cashew nut industry effluents, specifically two of its major phenolic components, cardol and cardanol. *Pan-American Journal of Aquatic Sciences*, **4**(3): pp 363-368.
24. Maria Lucilia dos Santos and Gouvan C. de Magalhaes. (1999). Utilization of Cashew Nut Shell Liquid from *anacardiumoccidentale* as starting Material for organic synthesis: A novel route to Lasiodiplodin from Cardols. *Journal of Brazilian Chemical Society,* **10**(1): pp 13-20.
25. Menon, A. R. R.; Pillai, C. K. S. and Mathew, A. G**.** (1985). Cashew nut shell liquid-its polymeric and other industrial products. *Journal of Science in Industrial research*, **44**: pp 324-338. 2381-2383.
26. Muizebelt, W. J., Hubert, J. C., Nielen, M. W. F., Klaasen, R. P., Zabel, K. H**.** (2000). Crosslink mechanisms of high-solids alkyd resins in the presence of reactive diluents. *Progress in Organic Coatings*, **40**(1-4): pp 121-130.
27. Muturi, P., and Arunga, O. R**.** (1988). Cashew nut shell liquid: a review of production and research in Kenya. *Tropical Science,***28***:* pp 201 - 218.
28. Muturi, P. (1984a). Coatings formulation from cashew nut shell liquid and their characteristics. *Kenya journal of Science and Technology*, **5** *(1 and 2)*:pp 53-61.
29. Ranjana, Y. and Deepak, S.(2008). Studies of cardanol based epoxidizednovalac resin and its blends. *Indian journal of Chemistry and Chemical technology*, **2**: pp 173-184.
30. Risfaheria, T. T. I., Nur, M. A and Illah, S**.** (2009). Isolation of Cardanol from Cashew Nut Shell Liquid using the vacuum distillation method. *Indonesian journal of Agriculture,***2**(1): pp 11-20.
31. Saeid, F and Somayeh, P. (2010). Decatungstodivanadogermanicheteropoly acid (H6GeW10V2O40.22H2O): A novel, green and reusable catalyst for efficient acetylation of alcohols and phenols under solvent‐free conditions. *European Journal of Chemistry*, **1** (4): pp 335‐340.
32. Satoru, E.(1978).Study of reactive diluent for air-dried alkyd paints**.** *Journal of Applied Polymer Science,***22**(1): pp253-65**.**

33. Tyman, J.H.P. (1973). Long chain phenols.Part III. Identification of the components of a novel phenolic fraction in *Anacardiumoccidentale*(cashew nut shell liquid) and synthesis of the saturated member. *Journal of chemical Society of Perkins Transport*. **1**: pp 1639-1647.
34. Ursula, B., Werner, B., Ralf, H., Willi, F and Jurgen, O. M.(2009). Esters of calendula oil and tung oil as reactive diluents for alkyd resins, *European journal of lipid Science and technology*, **112**: pp 103-109.
35. Wicks, Z. W., Jones, F. N. and Pappa, P. S**.** (1992).Organic Coatings: Science and Technology. 2ed. New York: Wiley-Interscience.
36. Zabel, K.H., Klaasen, R.P., Muizebelt, W.J., Gracey, B.P., Hallet C., Brooks, C.P. (1999). Design and incorporation of reactive diluents for air drying high solid alkyd paints. *Progress in organic coatings*, **35**(1-4): pp 255-264, Eiseviersequiol.
37. Zeno, W. W., Frank, N. J. and Peter, S. P. (2007). Science and technology. Organic coatings 3rd ed, pp 313, John Wiley and sons.