Metals and Mechanical Properties of some Coatings Exposed to Outdoor.

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Abstract: *The metal composition of five architectural and two automotive coatings were determined and the coatings exposed to outdoor conditions for 500h so as to monitor their tensile strength (TS). Young's modulus (YM) and elongation at break (EB) as well as gel content and density. The results showed that the mechanical properties are largely affected by total metal concentration of each coating. The coatings that had relatively high concentration of total metal content, gel content and density generally had greater mechanical properties. Significantly, for both types of coatings, the post-exposure mechanical properties were generally greater than the pre-exposure values. The mechanical properties generally ranked as RBG>CRG>CRB>UZR=UZB and for the automotives, CAY >CAG particularly after exposure largely in agreement with the order of initial total metal concentration.*

Keywords: *Tensile strength, Young's modulus, elongation at break, metal composition, gel content, density.*

I. Introduction

The mechanical properties of paint and coatings are of paramount importance in maintaining their protective and probably decorative functions during the service life (Strivens, 1987).The relatively high level of metal content in paints emanates from pigmentation using inorganic pigments containing metals such as lead in red lead, zinc in zinc octoate, copper from copper phythalocyanines green and blue pigments, titanium as in titanium oxide (Bleiner et al,2000). Pigmentation generally improves the physical characteristics of paint films and has   certain effect on autooxidation reactions that occur, for instance, in alkyd paints modified by unsaturated higher fatty acids(Kalenda and Menc,2007).There are also the well known polymerization initiators/catalysts such as the Lewis acids and alkali metal or their amides in cationic and anionic chain addition polymerization respectively as well as the well-known Z-N transition metal salts/organometallic compounds for coordination polymerization. Other sources of metals in paints include metal driers (siccatives) such as compounds of lead, cobalt, zinc, calcium, manganese (Tanase et al,2004, Wu et al,2004,van-Gorkum and Bouwman,2005,Oyman,et al 2005)..Extenders, such as, Barium sulphate and Calcium carbonate, are another source of metals in paints..The thought of the likely effect of these elements in the overall performance of coatings naturally arises and this provokes the present study. Paint performance is generally evaluated through determination of their mechanical properties. An appreciable level of mechanical properties is required for optimal performance of coatings. Related to these properties is the gel content and its development which must be relatively stable with time. The formation of the gel which occurs normally during oxidative drying is very much influenced by the presence of the metals [Turoti et al, 2010].This is clear from the fact that almost all driers contain the metals which include, Co, Pb, Fe, Mn, Ti, V, Cu, Zn and Al [Eva et al,2003].Since most of these metals do not sublime during the life span of the coating, their existence would be contributory towards the ultimate mechanical properties of the coatings. Such mechanical properties of paint films consist of the stress or strain that leads to plastic yield (irreversible deformation) or failure expressed in the cracking of the film. The variety of mechanical stresses and strains affecting the paint films by altering their mechanical properties occurs during service life.(Strivens,1987). Although there are some reported studies on metals as precursors for oxidative drying there are no monitoring studies that have been reported showing relationship between metal content and physicomechanical properties in coatings during life service as to be demonstrated in the present study.This study is therefore set to assess the effects of some metals which could affect the fundamental parameters such as gel content, density on the ultimate mechanical properties. Five architectural paints (referred herein as ACP) coded as, UZR, CAG, CAB,UZB and RBG and two automotive paints(referred herein as AUP) coded as: CAY and CAG, were employed for this study.

II. Experimental

Materials and Methods
The ACP and AUP samples were obtained from two paint shops in two major cities of Nigeria.

Preparation and aging of coatings.

The method employed is as detailed elsewhere [Turoti et al,2010].10.0cm^3 of previously homogenized liquid paint was applied onto a clean glass plate placed on a table at 180^0 and allowed to dry to constant weight at ambient temperature. Appropriate sizes of the dry film were carefully removed using new and clean razor blade before and after exposure to outdoor environment for 500hrs.They were lightly brushed to remove dust particles for each test analysis.

Determination of Elemental Concentration

The Energy dispersive X-RAY fluorescence (EDXRF), EclipseE spectrophotometer equipment Model XR-100CR was supplied by AMTEK, Inc.MA, USA, at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University (O.A.U),Ile-Ife was used.

Determination of mechanical properties

The Young's modulus (YM), tensile strength (TS) and elongation at break (EB, %) were determined using computerized Instron tensile tester model 33069(2006) at the Centre for Energy Research Development (CERD) Obafemi Awolowo University (OAU), Ile-Ife. Films of 3cm gauge length, 1cm width and similar thickness using BS micrometer screw gauge, were employed as reported elsewhere (Turoti et al,1999). A maximum shear load of 50kg with chart to cross head ratio of 4:1 and the cross-head speed of 10mm/min were used. The properties were computed or obtained directly from computer print out.

Determination of gel content

The procedure of determination was as detailed elsewhere[Turoti et al,2010].Prior to exposure 0.1g of each dry coating was added to 100g of purified kerosene, shaken and left for 72hr after which vacuum pump filtration was carried out The residue(gel) was dried to constant weight and the gel content determined by the expression:Gel content (%) = W_f/W_o x 100 Where W_o and W_f are the weights of initial paint sample(0.1g) and gel residue, respectively. The same procedure was repeated after exposure All determinations were carried out in triplicates and average calculated.

Determination of density of paint films

With the aid of a standard and calibrated ruler the length and width of each dry paint samples was measured several times and averaged for accuracy while the thickness was determined using micrometer screw gauge (BS) on several parts on each film and measurements averaged. The volume was calculated. The mass was obtained using Metler balance and the density (mass/volume) of each test paint film was determined as the mean of three determinations.

Correlation co-efficient between mechanical properties and elemental composition

A Pearson's correlation coefficient, r, software was used.

III.   Results and discussion

Table 1 shows the metal compositions and concentrations for

Table 1: Metal composition and concentration (w%) of paint samples

Metal	Concentration values in different paints (w, %)						
	UZR	RBG	CAG	CAB	UZB	CAG	CAY|
K	5.6857±0.2	4.2863±0.54	2.2498±0.0	3.071±0.13	6.4988±0.36	0.3193±0.1	0.3712±0.14
Ca	4.0425±0.2	2.1305±0.09	2.7297±0.0	15.36±0.28	0.2984±0.71	0.6687±0.1	29.012±0.09
Ti	0 0.52±0.26	24.423±0.01	2.7104±0.0	0.060±043	4.1659±0.01	26.8932±0.	29.412±0.09
Cr	2.5695±0.0	20.2677±0.01	0.0128±021	3.1164±0.0	0.0474±0.01	ND	0.4506±0.89
Mn	0.1201±0.0	0.1206±0.62	0.0262±0.2	0.0461±0.4	0.0366±0.73	0.1016±0.2	ND
Fe	13.139±0.2	7,5629±0.09	1.1159±0.3	0.8346±0.3	2.8149±0.12	2.9857±0.0	2.1600±0.01
Cu	1.0267±0.0	9.8148±0.01	12.466±0.0	4.3170±0.0	8.6718±0.01	0.0177±0.0	0.0188±0.01
Zn	3.1741±0.0	0.1054±0.01	0.4698±0.0	0.2403±0.0	0.5368±0.01	0.0164±0.0	0.0240±0,10
Co	1.3800±0.0	0.1258±0.01	3,5199±0.0	2.7250±0.0	2.2201±0.01	ND	ND
Ni	0.3775±0.0	16.540±0.01	14,522±0.0	12.563±0.0	11.629±0.01	ND	0.8763±0.92
Pb	7.2684±0.0	16.540±0.01	14,522±0.0	12.563±0.0	11,629±0.01	ND	0.8763±0.92

Σ=39.4139±17   ☐=65.711.42   ☐=40.41± 0.83   ☐=43.27±1.75   ☐=39.41± 1.41 ☐= 30.64±1.34 Σ33.98±162 of the five ACP and two AUP samples as well as the summation of all metaleach paint sample. The order of total metal concentration shows RBG>CAB>UZB=UZR>CAG for the ACP and CAY>CAG for the AUP. This could be attributed to the bulk property of the paint composite which may depend primarily on the metal particle distribution and concentration. Table 1 reveals that the RBG sample contains the highest amount of Ti and Pb metals at 24.423±0.01% and 16.540±0.01% respectively, among the ACP samples. Significant amounts of Ti are also present in the two automotive paints at 26.8952± 0.06 and 29.412± 0.09 % for the CAG

and CAY respectively and 0.8763±0.92 of Pb was detected only in CAY. All these paint samples are not white outwardly and unexpected to contain such significant levels of Ti. Some of these metals could have been incorporated into the paints for other functions. Figures 1and 2 show the bar charts for the TS of the ACP and AUP samples,
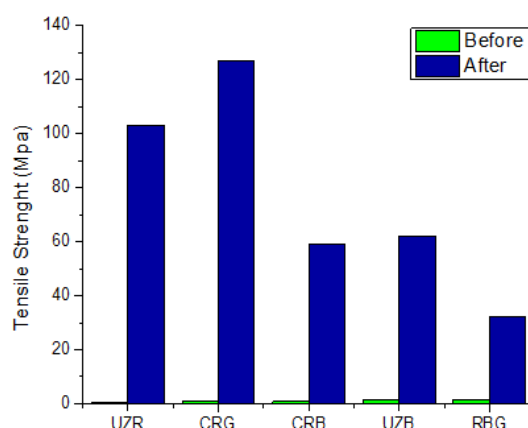
Fig.1.Tensile strength of decorative paints before and after 500h and after 500hrs outdoor exposure

It is clear that the values of TS after exposure are significantly greater than pre-exposure values UZR>CRG>UZB>CRB>RBG for ACP and CAY>CAG for the AUP samples. The YM also has greater values after than before exposure. However, in contrast to TS, the YM trend is RBG>UZB>CRB>CRG>UZR for the ACP(Fig.3) and CAY>CAG for the AUP samples (Fig.4) . The expected converse order of the EB(%) can be seen in Figs 5 & 6.Thus the coating films that have high YM have low EB in agreement with an earlier study(Turoti et al,2010) paints become stronger and stiffer as well as less flexible during the period of outdoor exposure. Similar trends are generally found for the AUP samples although the post-exposure EB are longer than the pre-exposure values.
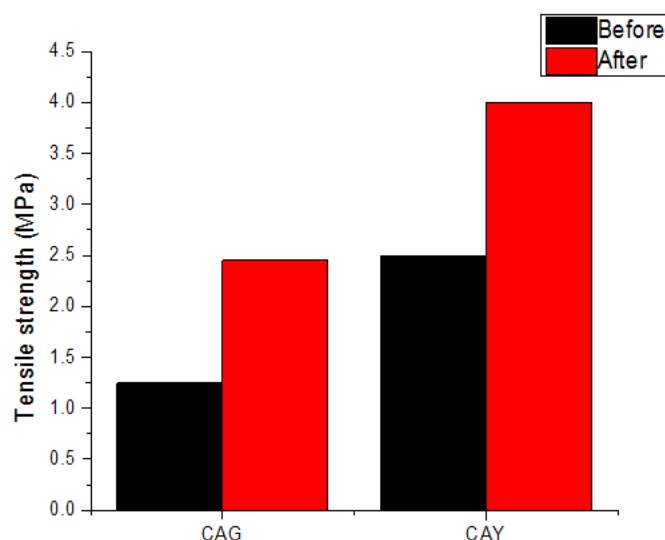
Fig.2.Tensile strength of AUP before and after 500hrs of outdoor exposure

The expected converse order of the EB(%)RBG<UZB<CAB<CAG<UZR for the ACP and CAY< CAG for the AUP can be seen in Figs.5 and 6.Thus coating samples that have high YM have low EB in agreement with an earlier study[Turoti et al,2010]. This could be explained by the fact that the outdoor exposure led to formation of oxygen containing cross-links between adjacent polymeric chains resulting into greater strength to stretch the chains per unit strain resulting into smaller strain for the applied stress giving the high YM and consequently shorter EB as exposure progresses, that is, RBG<UZB<CAB<CAG<UZR for the ACP and CAY< CAG for the AUP (see figs 5&6) .Thus the coatings become stronger and stiffer as well as less flexible during the period of outdoor exposure. Similar trends were generally found for the AUP samples although the post-exposure EB were longer than the pre-exposure values for each of the automobile coating samples. These interesting results where exposure to outdoor conditions
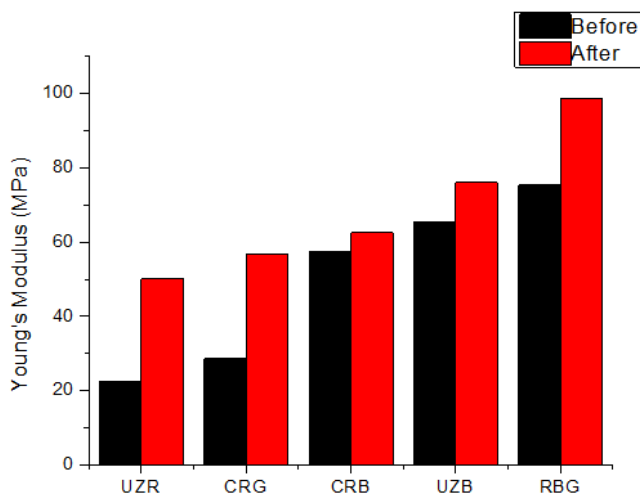
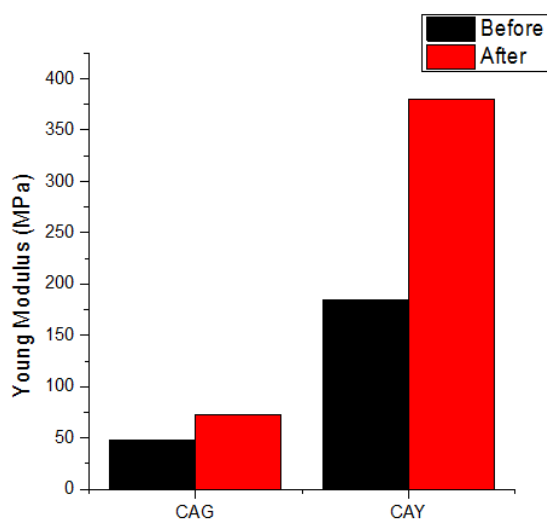**Fig.3.** Young's modulus of ACP before and after 500h of outdoor exposure

Fig.4: Young's modulus of AUP coatings before and after exposure.

Resulted in improved mechanical properties may not be unconnected with the presence of metallic components of the coating which could be incorporated to carry out functions which are multidimensional. For instance, Ti is available in greater concentration than many other metals in these colored paints and could be responsible for thermal stability and resistance to outdoor heat as well as atmospheric oxidation in line with a recent study (Sanchez-Moreno et al, 2014).This resistance lead to improved resistance to outdoor degradation necessary for enhanced mechanical properties.
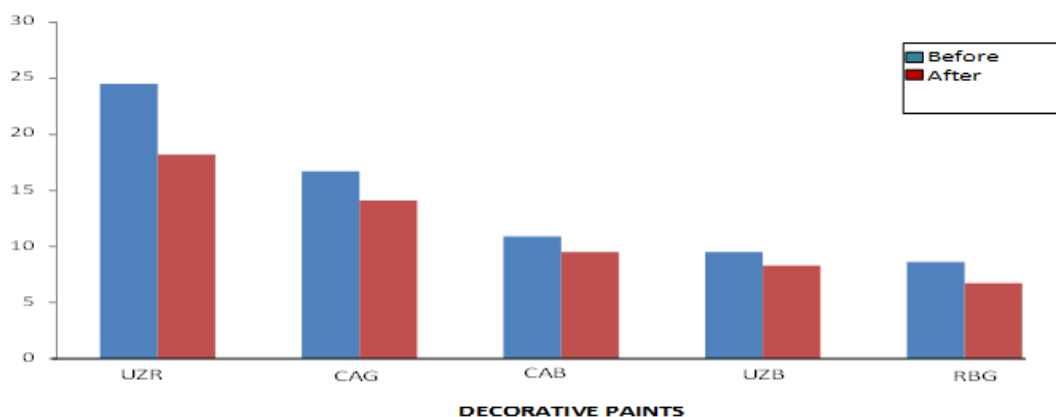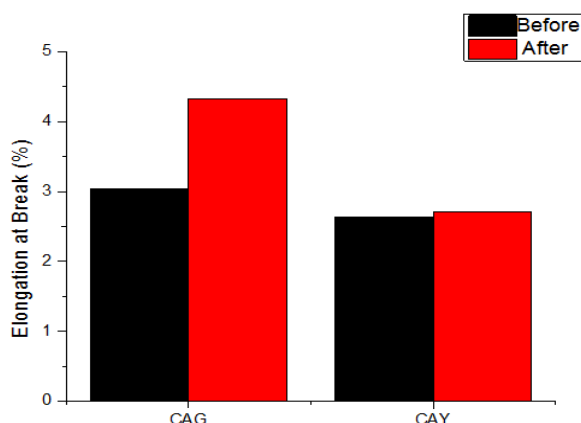

Fig.5: Elongation at break of ACP coatings before and after exposure.

Metal and that of the mechanical property for a paint sample. It can be seen that, at 0.05 significance level, there was positive correlation between each metal concentration and mechanical properties for a coating sample. it can be seen that, at 0.05 significance level, there was positive correlation between metal concentration and the mechanical properties of the coatings. This suggests the possibility of the metals participating in the formation of the fundamental gel structures responsible for the improvement of the mechanical properties during the outdoor exposure of the coating samples. Such structures could be the metal catalyzed and metal inserted cross-linked gel.

Fig.6. Elongation at break (%) of ACP before and after 500hr of outdoor exposure

Table 2 shows the statistical correlation between the total concentration of a metal and mechanical properties during the outdoor exposure of the coating samples. The relatively high correlation between some of the mechanical properties and metals may not be unconnected with their roles as through drier metal (K) and auxiliary drier metals (Ca and Zn) in the test coatings. Table 3 shows that the YM increases with the gel content of the ACP coatings while, as expected, the elongation at break has a converse relationship with the gel content. The TS also

Table 2: Correlation between Metal Composition and Mechanical Properties of Coatings.

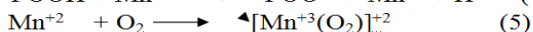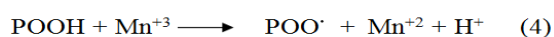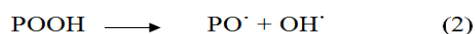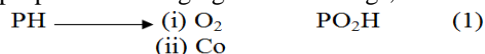| Metal	TS	YM	EB
K	0.745	0.137	0.393
Ca	0.745	0.508	0.64
Ti	0.483	0.134	0.670
Cr	0.982	0.096	0.054
Mn	0.387	0.101	0.658
Fe	0.081	0.305	0.730
Cu	0.0308	0.181	0.935
Zn	0.989	0.305	0.393
Co	0.086	0.579	0.103
Ni	0.508	0.213	0.006
Pb	0.243	0.554	0.772

has a positive correlation with the gel content. The ACP coatings have a pre-exposure gel content order of, RBG>UZB>CRB>CRG>UZR and for the AUP coatings samples, CAY>CAG. These findings are in agreement with an earlier work which showed direct relationship between gel content and YM [Turoti et al, 2010].The gel content of each coating at the end of 500h was 100% and shows that a possible mechanism for the gel formation was oxidative since the gel increased from lower values before exposure to higher values after exposure. In other words, the drying process must have probably occurred by oxidative process.

Table 3. Gel content (%) and Mechanical Properties before outdoor Exposure

Paint Sample	Gel content(%)	TS(Nm^{-2})	YM(MPa)	EB(%)
ACP				
UZR	20.2	0.50	27.45	73.84
CAB	22.5	0.72	28.56	50.00
CAG	24.5	0.84	57.46	32.56
UZR	28.4	1.22	65.45	28.45
RBG	29.2	1.54	75.32	25.90
AUP				
CAG	34.4	2.50	185.32	7.11
CAY	30.4	1.72	48.00	9.93

Post-exposure gel content=100% for each coating.

Table 4 shows that the density of each ACP sample increases during the 500h outdoor aging and also shows the same trend for the AUP coating samples.. The increase in density brings an increase in the TS and particularly YM along with the expected decrease in elongation at break in agreement with the reports in the earlier section. It is probably in order to state that the presence of the metals in the paints influenced the formation of the gel resulting into increased density with concomitant improvement in the TS and/or YM as well as reduction in the EB during the period of exposure of the coatings. With the detected metals in Table 1 and general observation that most of the test coatings are alkyds(from the labeling of the manufacturers on the containers), the following view may summarize the chemistry that results into the enhancement of mechanical properties with aging of the coatings, in line with the earlier workers (van-Gorkum,2005, Walltron et al,2003]

$$PH \xrightarrow{} \text{(i) } O_2 \quad\quad PO_2H \quad\quad (1)$$
$$\text{(ii) Co}$$

$$POOH \xrightarrow{} PO^{\cdot} + OH^{\cdot} \quad\quad (2)$$

$$POOH + Mn^{+2} \xrightarrow{} PO^{\cdot} + Mn^{+3} + OH^{-} \quad (3)$$

$$POOH + Mn^{+3} \xrightarrow{} POO^{\cdot} + Mn^{+2} + H^{+} \quad (4)$$

$$Mn^{+2} + O_2 \xrightarrow{} [Mn^{+3}(O_2)]^{+2} \quad\quad (5)$$

PH= Polymer

Both Co and Mn are detected in all the ACP samples and Mn present only in CAG of the two AUP samples. The possibility of these reactions is therefore expected. However, it has been demonstrated that while Co is more effective in catalyzing hydroperoxidation, Mn is more effective in catalyzing decomposition of the hydroperoxide as shown in the equation (1) for Co andequations (3) & (4) for Mn (Tuck,2000).Equations (3) and (5) explain the process leading to the formation of P-O- M-O-P crosslinks during drying of coatings .Other common transition metals capable of hydroperoxide decomposition include Fe, Cu and Ti (Schaich,2001). These primary metal driers are aided by the through metal driers such as Pb and auxiliary metal dryers including K, Ca and Zn (Walltron,2003) which are present in both the ACP and AUP coatings (see Table 1). When a coating dries the action of driers does not end when a coating dries as the process continues throughout the life span of the coating culminating in embrittlement (Wiskeman, 2000).This may suggest why the ACP and AUP contain relatively high level of Ti or Pb to ensure continuity of drying for the overall enhancement of physical and mechanical properties of the coatings. Most of these metals that have relatively high % composition are not utilized as pigment components. For instance, Ti, usually from the white pigment,TiO_2 is present in each of these coatings in very significant quantities yet none of the paint samples used in this study was white (Table 1).The possibility of adding Ti so as to execute other important function such as light scattering(to disallow light from being absorbed by the coating so as to reduce degradation by solar UVB)and improvement in opacity may not be ruled out. In this study, all the paint samples containing high Ti content have good mechanical properties, high cross-inked gel and density. For instance, the YM of RBG and CAY are more improved with highest Ti content while those with lower Ti have smaller values of YM and other properties. It is most probable that there are more impact on the mechanical properties in paint samples that contains higher quantities of some of these metals (Table 1).It is a common view that pigmentation in commercial paints can be effected rarely by single or mostly by mixed pigments containing two or more metals capable of performing many functions apart from pigmentation. For instance, while a blue sample will contain primarily copper pthalocyanine blue (see Table 1) it may be combined with other blue pigments, for example, iron blue (Prussian blue) containing K and Fe and Cobalt blue pigment whose formula is Cobalt chromium aluminate. Thus a gamut of metals in varying quantities are expected in a paint sample as can be seen in Table 1.Also it is known that many other additives containing many metals are part of paint formulation carrying out other essential functions in the paint. All these metals contribute immensely to the mechanical properties of the paint. Table 4 shows slight increase in density (ρ) of dry coatings before and after aging and gives evidence for the decrease in free volume during drying of the coatings arising from the crosslinking of the polymer chains as discussed earlier.

Table 4: Effect of Aging on Density of ACP and AUP Coating Samples.

Coating Sample	Density in gcm^{-1}	
	Before	After
ACP		
UZR	1.45	1.64
CRG	1.65	1.73
CRB	1.77	1.84
UZB	1.87	1.90
RBG	2.97	3.00
AUP		
CAG	2.75	3.12
CAY	2.15	2.95

It is obvious from Table 4 that the order of residual density before and after exposure is generally of the order, UZR<CRG<CRB<UZB<RBG for the ACP samples, and CAY<CAG for the AUP samples. It is probably convenient to state that the greater the pre -exposure density the greater the post-exposure values and the converse is true from this result. The result in Table 4 largely agrees with the mechanical properties obtained in the earlier section of this report. As density value slightly increases from the pre- to post-exposure values, for each paint sample, the YM also increases and flexibility decreases. Paint sample with high or low gel (cross-linking) content value also has low density and high or low values of TS and YM respectively(Table 3).The presence of metals has been indicted to be responsible for the cross-linked gel and it is reasonable to adduce that the metals also effect the density of the paint samples. The ability of a paint sample possessing adequate metal content affects the development of gel content and density of the dry coatings that influence the values of mechanical properties. In this study, the coating sample that has high metal content generally possesses high cross-link density, high YM, toughness and decreased flexibility and resistance to rapid deformation in line with an earlier work(Shenoy and D' Melo D.J,2006).

Acknowledgement

Conclusion
This study has shown that outdoor aging of both architectural and automotive coatings generally resulted into increases in both the Young's modulus and tensile strength and decreases in the elongation at break. There is increasing formation of metal catalyzed and inserted oxygen cross-linked gel between the polymer chains. The greater the amount of some metals the greater the gel content and density of the coating resulting into improved mechanical properties.

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