International Journal of Sciences

Research Article Volume 6 – February 2017 (02)

Effects of UV on Ageing Properties of some Nail Polishes, Acrylic Emulsions and Gloss Paints

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Abstract: Photo-degradation stability of most commonly used nail polishes, acrylic paint emulsions and gloss paints have been investigated. The paints investigated in this study were nail polishes red (17), wine (23, 36 and 92), pink (26, 39 and 80). Lilaic (52), purple (16), golden (43) made by Yimei Commodities co; Ltd and acrylic emulsions 7084 (Pacific Blue), 3040 (Cream) and 9999 (Brilliant White) and gloss paints 7084, 3040 and 9102G (Brilliant White) made by Fine Coat. The Dry to Touch time, weight loss of the paint film, discolouration and structural changes of the paints subjected to UV irradiation in an accelerated ageing chamber were determined at 0, 100, 150, 200 and 300 hours of UV irradiation making use of gravimetry, colorimetry and FT-IR Spectroscopy. Results show Dry to touch time for nail polishes to be less than 2 minutes, 30 minutes for acrylic emulsions and about 60 minutes for gloss paints. Weight loss observed was in the order Pacific blues > Brilliant white > Cream. There was no significant weight loss for the Nail polishes. Colorimetric measurements indicated the reduction in the absorption of visible light and discolouration and loss of gloss was evident in the blue paint more than others. Increase in absorbance was observed for all nail polishes with the exception of Red (17) and the application of Varnish (V_{45}) to the nail polishes inhibited discolouration. FT-IR spectroscopy showed that Pacific Blue 7084, followed by Brilliant White 9999 and Cream 3040 showed most structural changes. There was the reduction of transmission peak at 2900 cm^{-1}, (symmetric stretching of C-H bond), 1823 cm^{-1}, 1731 cm^{-1} (C=O,) and disappearance of 1625 cm^{-1} (C=C) and 2925 cm^{-1}(C-H stretching) which was noteworthy. Similar results were obtained for the nail polish. In conclusion, the samples of the paints analyzed were not stable to UV radiation. Weight loss occurred to samples which were treated to accelerated ageing procedures hence, paints aged faster on exposure to UV radiation. Application of varnish onto the surface of nail polish inhibited discolouration and slowed down ageing. Pacific blue paints aged faster than other colours.

Keywords: Acrylic emulsion paints, Gloss paints, Nail polishes, Accelerated ageing, Colorimetry, FT-IR spectroscopy, Photo-degradation

Introduction

Paints have been manufactured since prehistoric times, but until recently they were highly expensive and thus were mainly used for artwork. It is only since the nineteenth century that houses have commonly been painted. Today paints are used for colouring, decoration and protecting many surfaces, including houses, cars, fingernails, road markings, underground storage vessels, electrical and electronic appliances, clothing, building structures, etc. Paint is essentially composed of a binder, pigment and solvent. These compositions vary from one paint to another and behave differently towards climatic conditions which vary with locations and may have adverse effects on paints.

Polymers based on drying oil, nitro-cellulose, acrylic and methacrylic esters are widely used in the formulation of varnishes, paints, adhesives, and, more specifically, of protective coatings for different surfaces [1-3]. Acrylic paints, containing suspended pigment in the emulsion of acrylic/methacrylic polymers, are quick-drying paints which have a water-soluble property, but convert to a water-resistant film [4-6] after drying. Gloss paints contained pigment dissolved in drying oil and suitable solvent, this is a slow drying paints compared to acrylic paints while nail polishes are usually made up of binder such as nitro-cellulose, acetate, etc and pigment in a suitable volatile organic solvent. [7]

Paintings, exhibited or stored, are susceptible to environmental factors, and destructions occur with the passage of time. To protect these coated surfaces and art works, the reactions of the materials with

Published at: http://www.ijsciences.com/pub/issue/2017-02/
DOI: 10.18483/ijSci.1190; Online ISSN: 2305-3925; Print ISSN: 2410-4477

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these destructive factors should be clarified. In this frame, the impact of ultraviolet irradiation, humidity, and temperature on the painting's chromatic structure have been found to be of primary importance [8, 9]. Given the increasing and varied application of paints, it is necessary to evaluate their stability against destructive factors such as sun light [10, 11].

The process of natural ageing of painting materials could be reproduced in the laboratory only by considering a simplified approach through some kind of simulation with convenient short-term experiments. Lifetime provision and mechanistic studies of the outdoor destruction processes are generally carried out by the help of accelerated ageing experiments including UV light and/or temperature studies. The light sources which could be efficiently employed for such purposes should have high power output and the closest resemblance to the solar light spectrum, particularly in the UV range [12, 13].

Polymers exposed to ultraviolet light are vulnerable to random degradation by light (photo degradation) and from oxygen effects catalyzed by light (photo-oxidation.). Durability of acrylic films exposed to UV light has already been investigated and the results show that acrylate units (which are reactive to oxidation and prone to chain-scissions) and long ester groups by promoting cross-linking reactions were the main cause of molecular and structural changes [2, 3]. For gloss paints, ageing process has been discovered to proceed via photo-oxidation of carbonyl group(s) or olefinic carbons or tertiary hydrogen atoms to form peroxides and hydroperoxides which can be broken down by light, heat or catalyst which makes the reactions self-propagating [14]. In a related work, Chiantore and Lazzari have studied structural and molecular changes under condition of accelerated aging and the results showed that molecular weight changes in all samples are due to the chain scission and/or coupling of macro-radicals [3]. The authors concluded that oxidation of polymers are strongly influenced by side groups such as butyl or isobutyl. Also, the light fastness declarations of three acrylic colors, i.e. cadmium red, ultramarine blue and chromium oxide green from different companies were investigated before and after UV exposure by Py–GC/MS, FTIR–ATR analyses, and color measurements [15]. The authors have detected different volatile compounds or new chemicals as oxidation products, due to weathering factors which vary with locations and have adverse effects on paints.

The aim of this work was to explore the effects of UV on ageing properties of most widely used nail polishes, acrylic emulsions and gloss paints. The selected paints including red, wine, pink, lilaic, purple, golden made by Yimei Commodities co; Ltd and acrylic emulsions 7084 (Pacific Blue), 3040 (Cream) and 9999 (Brilliant White) and gloss paints 7084, 3040 and 9102G (Brilliant White) made by Fine Coat were prepared in the form of a thin film, and exposed to the UV light in a photo-ageing chamber. After photo-ageing for 100, 150, 200 and 300 hours, samples were weighed and then analyzed using colorimetry and FT-IR spectroscopy.

Materials and Methods

Sampling

For this study, six widely used house-hold paints in Nigeria were selected. These paints were manufactured under the trade name FINE COAT by Chemstar Paints Industry (NIG) Ltd. Three of these paints are acrylic emulsion (water based) while the other three are Gloss (oil-based paints). Names of these paints are listed in Table 1.

Table 1: Names of selected paints.

No	Commercial Name
1	Brilliant White (9999), Acrylic Emulsion
2	Pacific Blue (7084), Acrylic Emulsion
3	Cream (3040), Acrylic Emulsion
4	Brilliant White (9102G), Gloss
5	Pacific Blue (7084), Gloss
6	Cream (3040), Gloss

For nail polish, ten most frequently used nail polishes were purchased from Aleshinloye Market in Ibadan. The nail polishes were manufactured by Yimei Commodities co; Ltd. The Colour and colour number of the nail polishes are listed in Table 2

Sample preparation

Coating of household paint

Samples of the paints were stirred thoroughly and were used as supplied. Coating process was carried out by brushing the samples of the paints on casted and plastered plywoods (2 x 5 inches). The surfaces were coated three times leaving it to dry to touch each time before applying the next coat at 18^{o}C. Painted wall-like plywoods were left in the dark for 14 days until the curing process was completed.

Table 2: Colour and colour number of the selected Nail Polishes

No	Nail Polish	Cosmetic Colour Number
1	Red (R_{17})	17
2	Wine (W_{92})	92
3	Wine (W_{36})	36
4	Wine (W_{23})	23
5	Pink (Pi_{80})	80
6	Pink (Pi_{39})	39
7	Lilaic (Li_{52})	52
8	Purple (P_{16})	16
9	Gold (G_{43})	43
10	Pink (Pi_{26})	26

Coating of nail polish

The samples were thoroughly shaken and two coating of each nail polish was applied on each acrylic nail tip at 18°C. The first coating was applied and left until polish applied was dry to touch before the next one. Varnish was then applied on 50% of the nail tip for each colour while 50% was left without varnish.

Accelerated photo-ageing

Prepared samples were exposed to UV irradiation at 0, 100 150, 200 and 300 hours of exposure in an accelerated photo-ageing chamber emitting at around ~254 nm. The photo-ageing chamber was equipped with two 20W UV lamp (λ~254 nm, Sunnew, China). The maximum temperature in the UV chamber during the experiments was around 30°C and the distance between the lamp and the samples was adjusted to 15cm.

Determination of weight loss on drying and absorbance reduction

Weight loss of the samples was measured by a digital balance (OHAUS Analytical Balance) with precision: ± 0.0001 g. Two series of the samples were prepared to be exposed to UV irradiation for 0, 100, 150, 200 and 300 hours. The weight loss of the paint films was determined gravimetrically at the defined intervals. A JENWAY 6505 UV / Vis Spectrophotometer was used to measure the discoloration rate of the samples in the characteristic wavelength of each paint maximum absorbance. FT-IR spectra of the samples were also recorded in transmission mode before and after defined intervals using a PerkinElmer Spectrum 100 Series FT-IR spectrometer with 4 cm^{-1} resolution in the range of 4000-400 cm^{-1}.

The expression below was used to calculate % weight loss and Absorbance Reduction (%) for each paint sample.

Quantification of Discoloration of paints samples under UV irradiation

To quantify the discoloration of the paint samples under the irradiation of UV light, a specific amount of the irradiated paint was soaked in 5ml of chloroform for household paints and 5ml of acetone for nail polishes and then, the absorbance of the solution was measured in the characteristic wavelength of the paints (pacific blue 625nm, cream 420nm, Wine, Liliac, Purple 520nm, Golden 434nm, Red 500, Pink 530nm)

- % weight loss = $\frac{Wo - Wt}{Wo} X100\%$
- Absorbance Reduction = $\frac{Ao - At}{Ao} X100\%$

Where W_o = weight of paint`s film (g) at time, t = 0 hour or weight of the control

W_t = weight of paint`s film (g) at time, t =t (t = 100,150,200,300 hours)

A_o = Absorbance of the paint sample (nm) at time, t = 0 or of the control.

A_t = Absorbance of the paint sample (nm) at time, t = t (t = 100, 150,200,300 hours)

Results and Discussion

Photo-degradation stability of most commonly used nail polishes, acrylic paint emulsions and gloss paints have been investigated by means of an accelerated photo-ageing chamber. Three different analysis methods, i.e. FT-IR spectroscopy, colorimetry and gravimetric analysis were used to evaluate the effect of UV light on thin films of the selected paints.

Drying Time

During coating process, it was observed that it took 30 minutes for acrylic emulsion paints to dry to touch while it took 60 minutes for the gloss paint and < 2 minutes for nail polish at 18°C

Weight loss measurements

The results are shown in the Tables below.

Table 3: Percent weight loss of acrylic emulsion and gloss paints with UV irradiation.

S/N	Paint Sample	100 hrs	200 hrs	300 hrs
1	PB(7084),AE	25.74%	35.20%	38.04%
2	C(3040),AE	12.04%	15.63%	20.92%
3	BW(9999),AE	20.49%	35.14%	40.58%
4	PB(7084), Gloss	73.68%	95.32%	98.03%
5	C(3040), Gloss	25.60%	58.10%	76.75%
6	BW(9102G),Gloss	71.26%	88.98%	91.19%

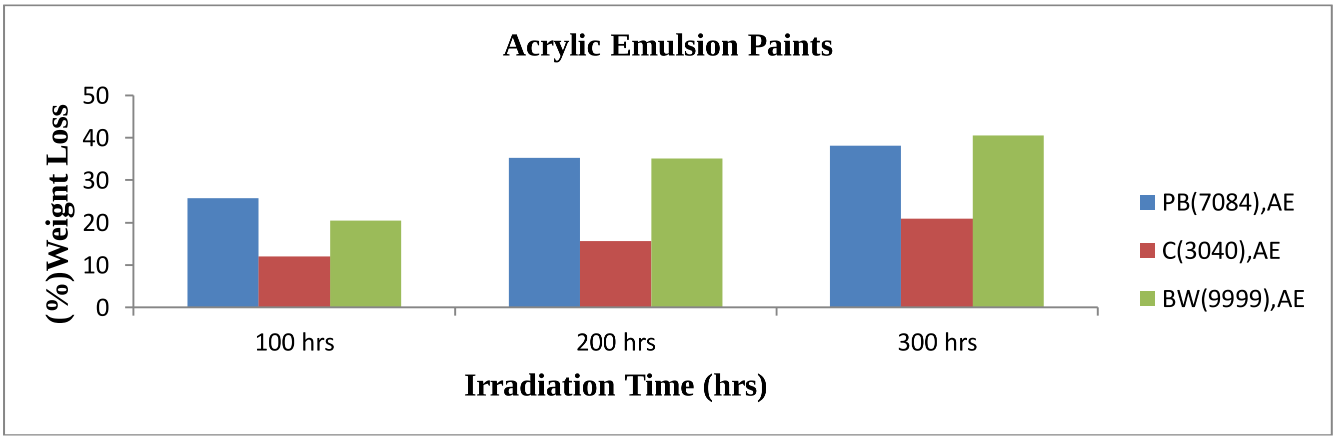


Figure 1: Graphical representation of the percent weight loss analysis of acrylic emulsion paints with UV irradiation.

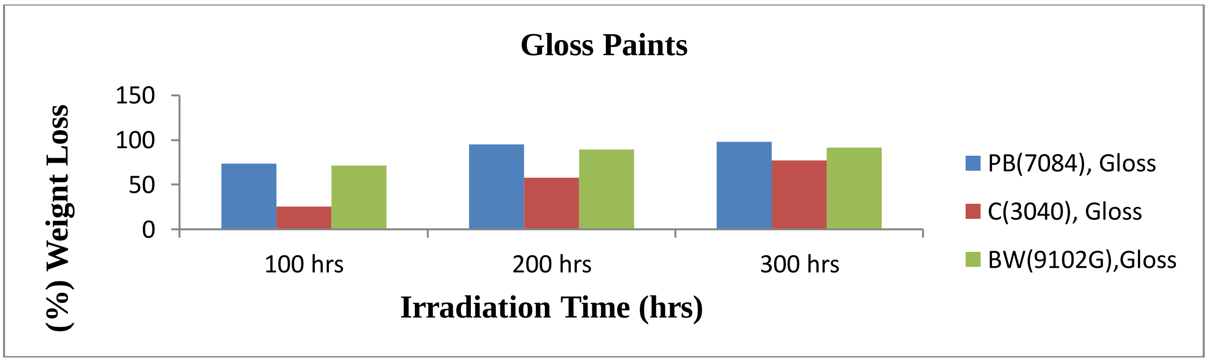


Figure 2: Graphical representation of the weight loss analysis of gloss paints with UV irradiation.

The results shown in Table 3 and figure 1 and 2 revealed decrease in % weight loss in the order Pacific Blue > White Brilliant > Cream. Acrylic emulsion paints compared to gloss paints have lower % weight loss and Cream (3040) acrylic emulsion paint was the most UV-resistant paint in the study.

Table 4: Percent weight loss analysis of nail polish with UV irradiation.

Sample	%weight loss at 150 hours for Uv	%weight loss at 150 hours for V	%weight loss at 300 hours for Uv	%weight loss at 300 hours for V
Pi_{26}	3.41	0.36	4.44	2.51
G_{43}	2.55	4.92	3.54	13.50
Li_{52}	0.15	1.73	3.83	5.15
Pi_{39}	0.14	1.49	4.85	4.71
R_{17}	0.81	0.43	7.43	4.04
Pi_{80}	0.65	0.41	4.84	2.72
W_{23}	0.28	1.01	3.22	3.95
W_{92}	0.15	1.32	5.49	6.11
Pu_{16}	1.62	0.00	5.99	4.81
W_{36}	0.34	1.06	4.00	4.93

NOTE: Uv= Unvarnished, V= Varnished

Generally, from Table 4 increase in % weight loss was observed for all varnished wine nail polish and this was also true for varnished golden nail polish when compared to unvarnished. For the other polishes, there was a decrease in % weight loss when compared to unvarnished. Here, varnish nail lacquer on varnished paints act as protective covering against UV radiation while unvarnished paints are subject to UV radiation effects.

Colorimetry

Acrylic emulsion and Gloss paints

Table 5 below shows the results of the (%) absorbance reduction.

Table 5: % Absorbance reduction at 100 hrs, 200 hrs, 300 hrs of UV irradiation for Paints

S/N	Paint Sample	100 hrs	200 hrs	300 hrs
1	PB(7084),AE	20.26%	45.96%	88.04%
2	C(3040),AE	17.43%	24.72%	55.54%
3	PB(7084),Gloss	61.94%	78.73%	95.52%
4	C(3040),Gloss	22.56%	53.81%	62.21%

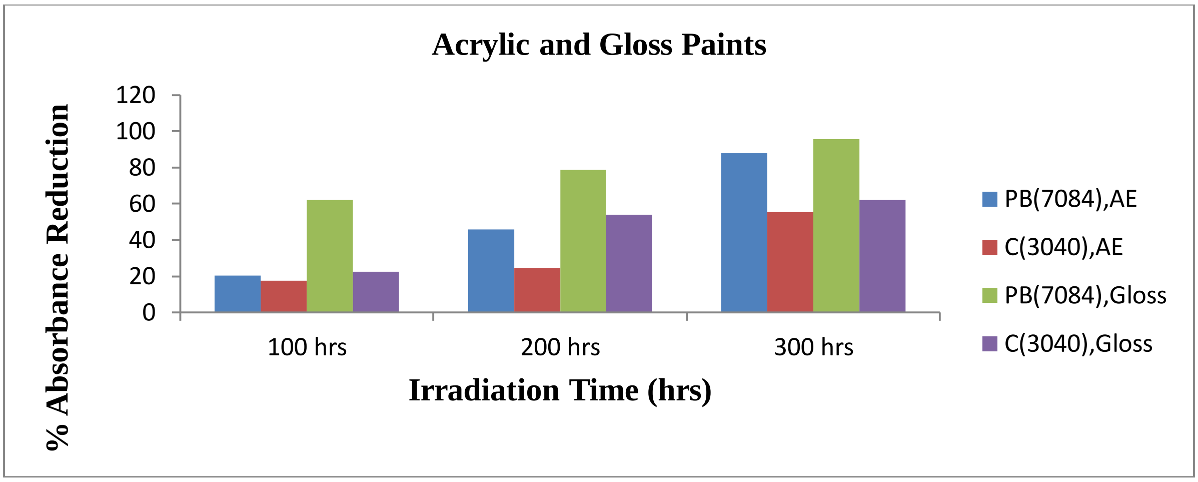


Figure 3: Comparative % absorbance reduction of the paint samples as a function of irradiation time.

From Table 5 and Figure 3, it was discovered that PB (7084) Gloss, has the highest % absorbance reduction (95.52%), followed by PB (7084) AE, (88.04%) while C (3040)AE, has 55.54%. Hence, C(3040)AE is the most UV resistant paint in current study. Discoloration observed here as a function of % absorbance reduction may be due to the photo-oxidation of the pigments present in the formulation of the paints.

Nail Polish

Table 6 and Figures 4 and 5 below show the results of the absorbance increase (%) with UV irradiation.

Table 6: Absorbance increase (%) analysis of the nail polish with UV irradiation at 150 hours and 300 hours

Sample	% absorbance increase at 150 hours for Uv	% absorbance increase at 150 hours for V	%absorbance increase at 300 hours for Uv	%absorbance increase at 300 hours for V
Pi_{26}	28.25	14.28	42.83	19.50
G_{43}	30.33	3.46	66.03	15.66
Li_{52}	68.82	63.16	67.54	58.56
Pi_{39}	23.86	20.24	85.87	61.60
R_{17}	-27.66	-34.30	-59.98	-47.16
Pi_{80}	36.50	23.95	40.14	37.18
W_{23}	36.33	28.86	79.16	70.88
W_{92}	38.17	24.03	70.96	69.45
Pu_{16}	57.87	42.61	87.31	51.48
W_{36}	54.97	25.65	61.29	41.36

NOTE: Uv= Unvarnished, V= Varnished

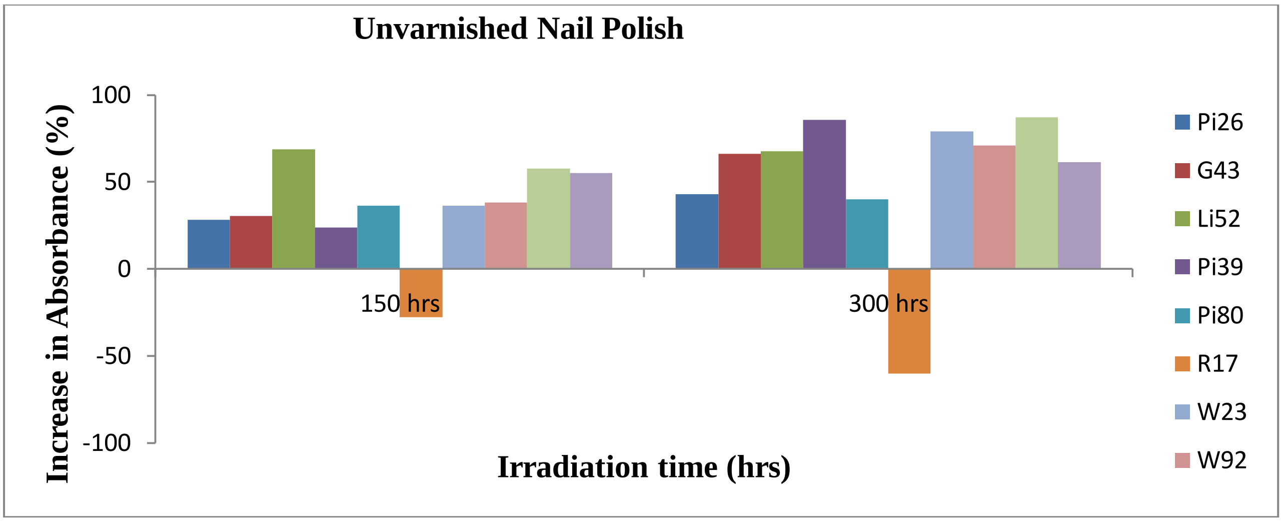


Figure 4: Percent increase in absorbance of the unvarnished nail polish samples as a function of irradiation time.

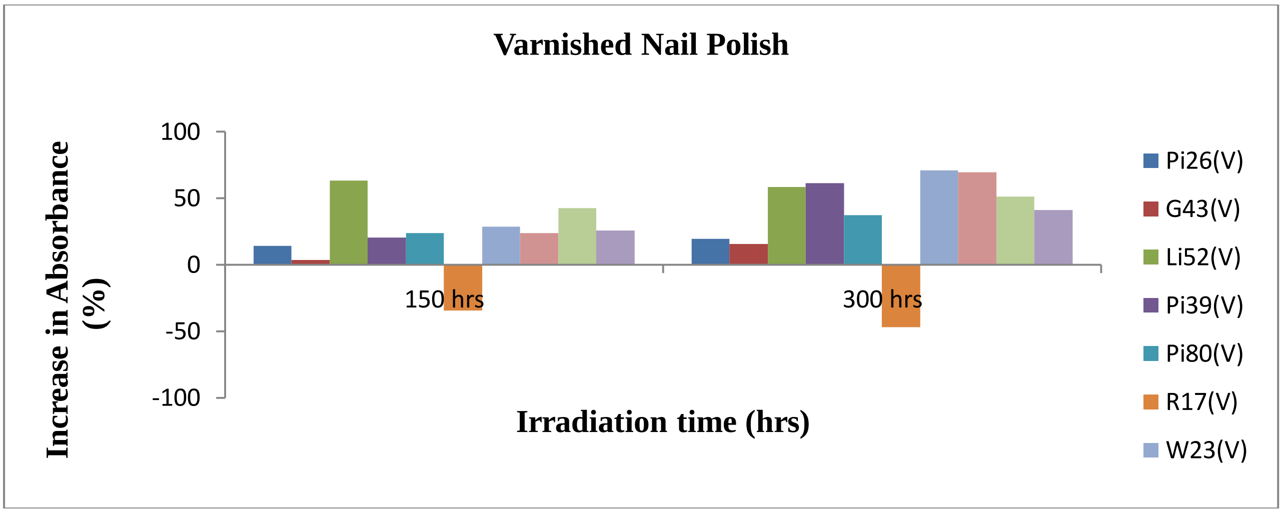


Figure 5: Percent increase in absorbance of the varnished nail polish samples as a function of irradiation time.

Generally increase in % absorbance was observed instead of absorbance reduction (%).

The absorbance increase observed for all the nail polishes except R_{17} may be due to the presence of transition metal (Fe and Mn) ions in the pigments. The metal ions may undergo oxidation reaction in the presence of UV light as a catalyst i.e. photo-catalyzed reaction, resulting in a more colored higher oxidation state of the transition metals.

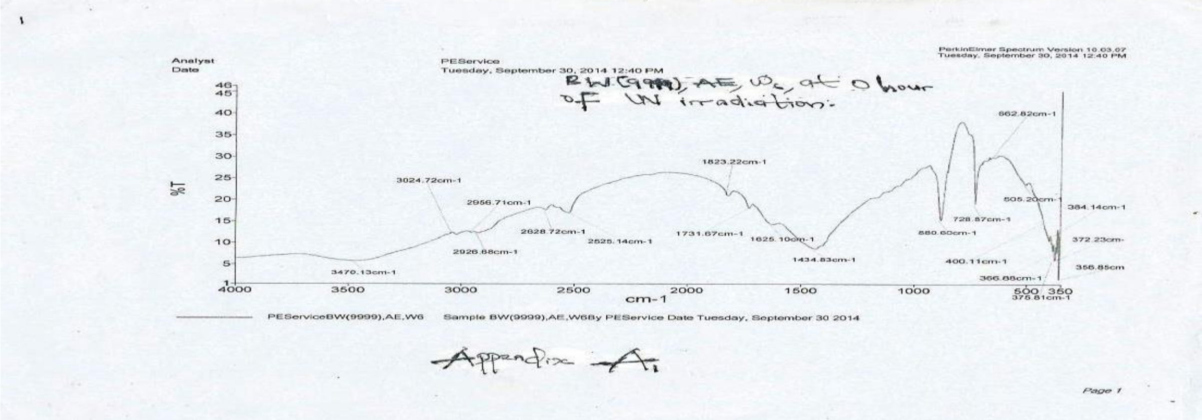
There was higher % increase in absorbance for unvarnished nail polish samples compared to varnished, this suggests that varnish lacquer on paint samples act as protective covering against UV radiation.

Absorbance reduction (%) which was observed for R_{17}, may be as a result of organic pigment in its formulation that is photo-degraded under UV irradiation.

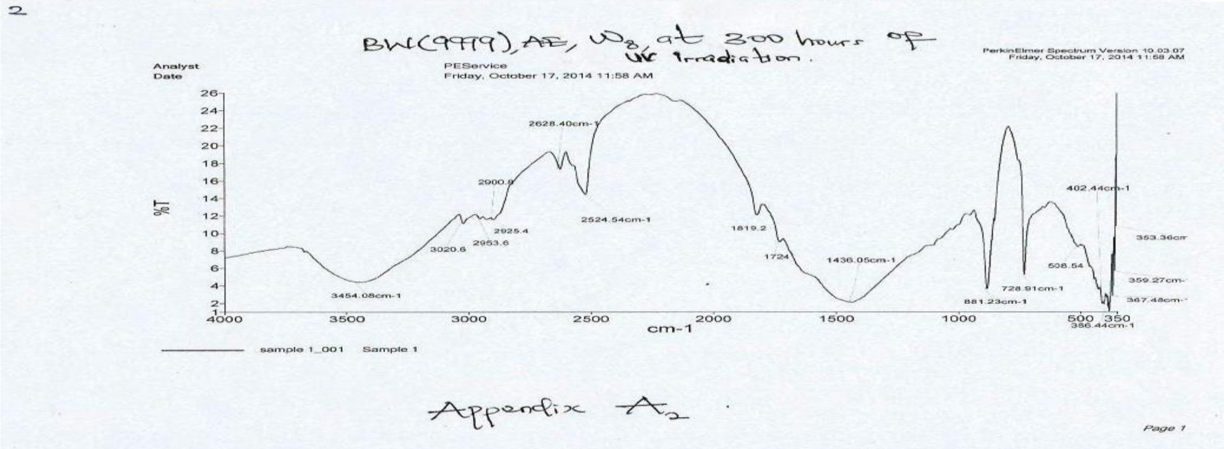
FT-IR Spectroscopy

The FT-IR spectra of the selected paints were recorded to study the structural changes of the paints under UV irradiation. The FT-IR spectra of paint films show that hydroxyl groups (mostly alcohols and peroxides), carbonyl and olefinic groups are responsible for the photo-degradation process.

Acrylic Emulsion and Gloss Paints

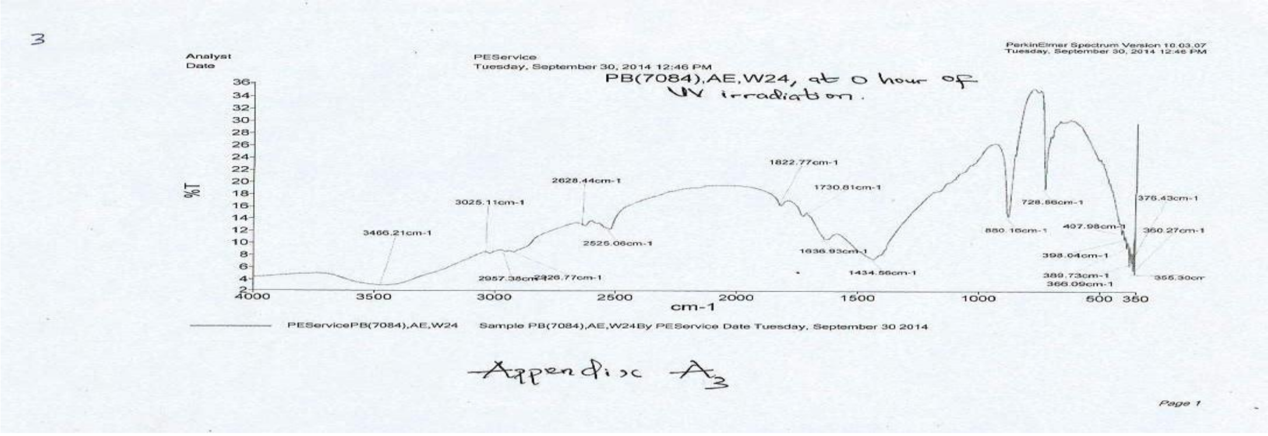


Appendix A1

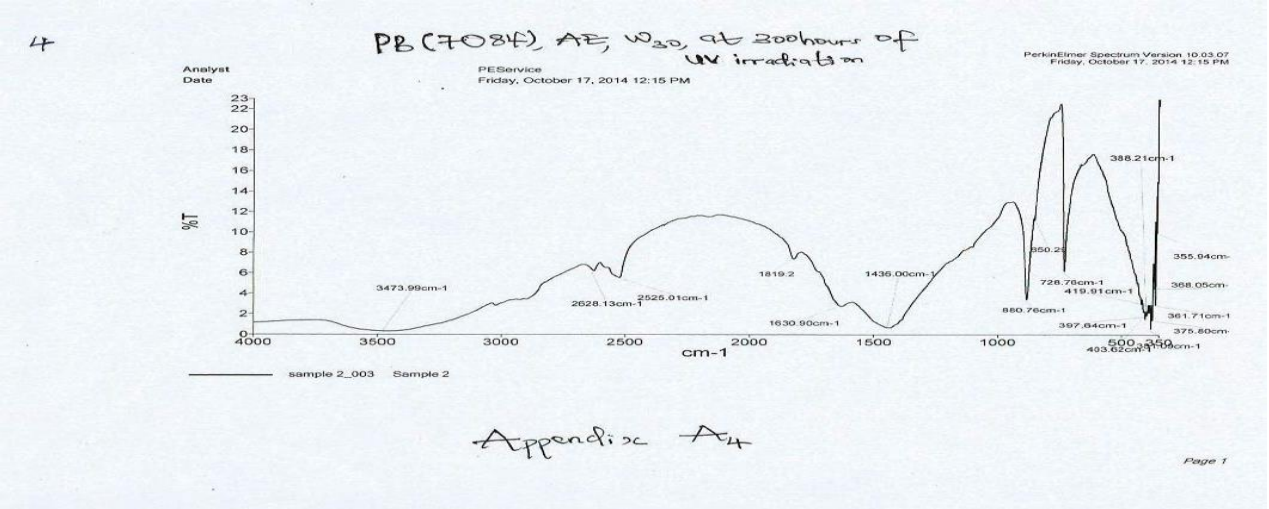


Appendix A2

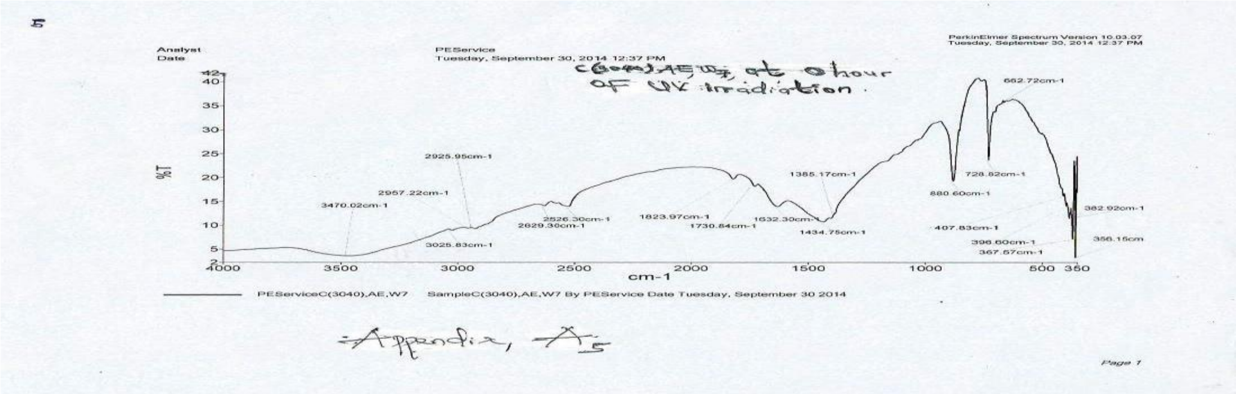
For BW(9999)AE, the peaks at 3470.13cm^{-1} and 3454.08 cm^{-1} are hydroxyl groups (mostly alcohols and peroxides). The reduction observed in the peaks is due to photo-oxidation of the acrylic polymer. 2900.8 cm^{-1} peak that newly appeared at 300 hours spectra is due to oxidation of C-H bonds resulting from photo-degradation products. The disappearance of 1625.10cm^{-1} of C=C is mainly due to auto-oxidation reaction of the acrylic polymer i.e. it act as the site for radical polymerization. Reduction in C=O peaks is due to cross-linking and chain scission during accelerated ageing.

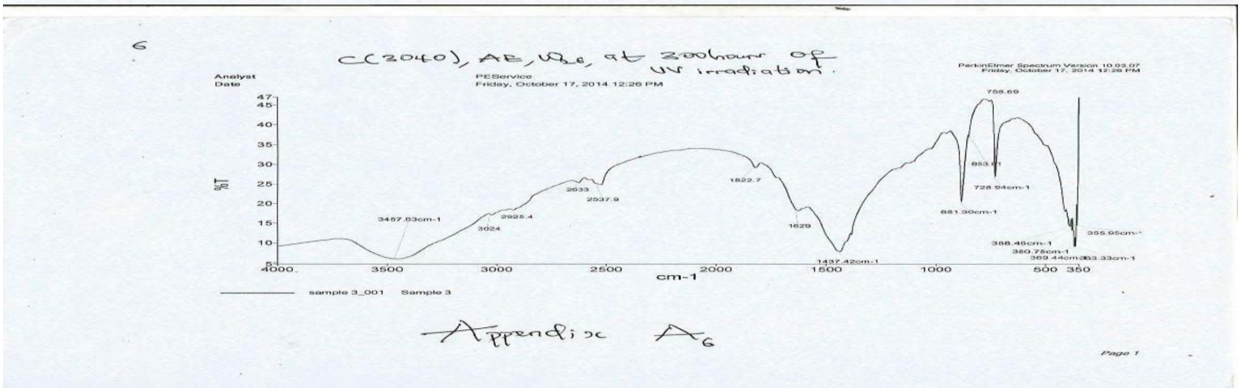


Appendix A3

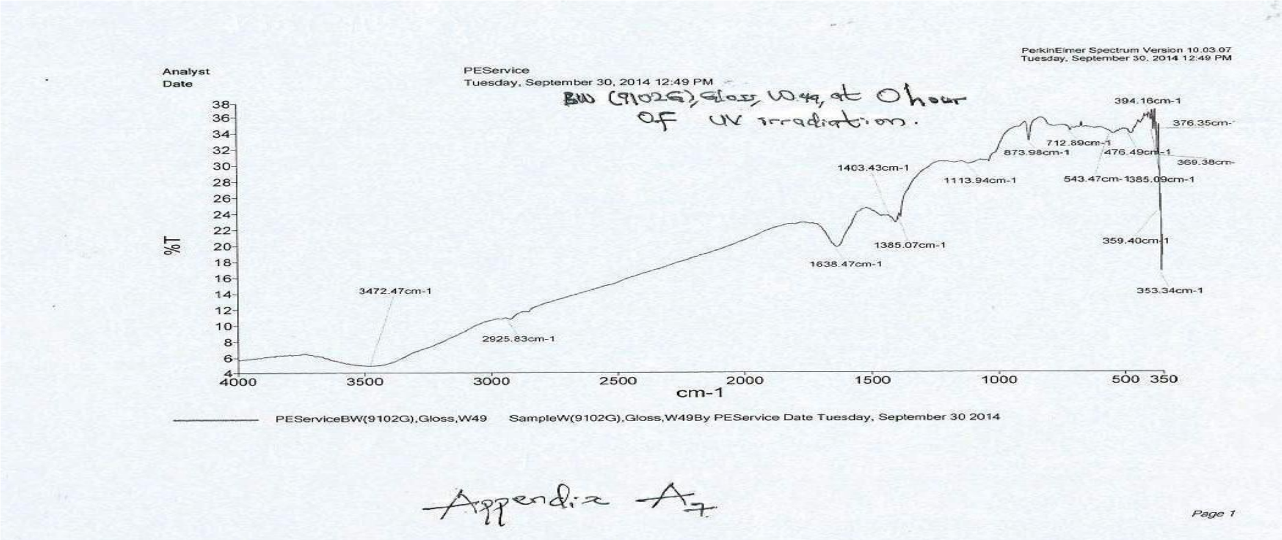


FOR both PB(7084),AE,W24, at 0 hour of UV irradiation and PB(7084),AE,W30, at 300 hour of UV irradiation, similar spectra peaks are observed as above, except for 1636.93 cm^{-1}(0 hour) and 1630.90(300 hours), which are the peaks of C=C bonds from pigment and the reduction of these peaks with irradiation time is as result of pigment degradation. Also, there was a disappearance of C=O peak at 1730.81cm^{-1}, when compared with 300 hours spectra, this is as result of cross-linking and chain scission of acrylic polymer undergo as photo-oxidation process to form lower molecular weight VOCs.

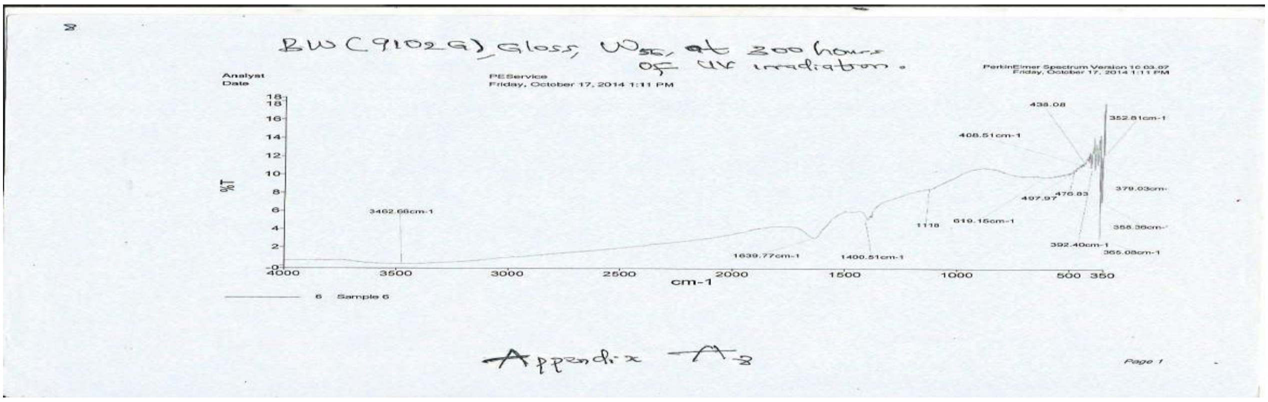




After 300 hours irradiation, the OH peak at 3470.0 cm^{-1} of C(3040)AE disappeared and a new strong broad peak appeared at 3457.6 cm^{-1}. This may be due to the formation of peroxides during the ageing process. Similarly, the C=O peak at 1730.8 cm^{-1} disappeared probably due to acrylic polymer photo-degradation.

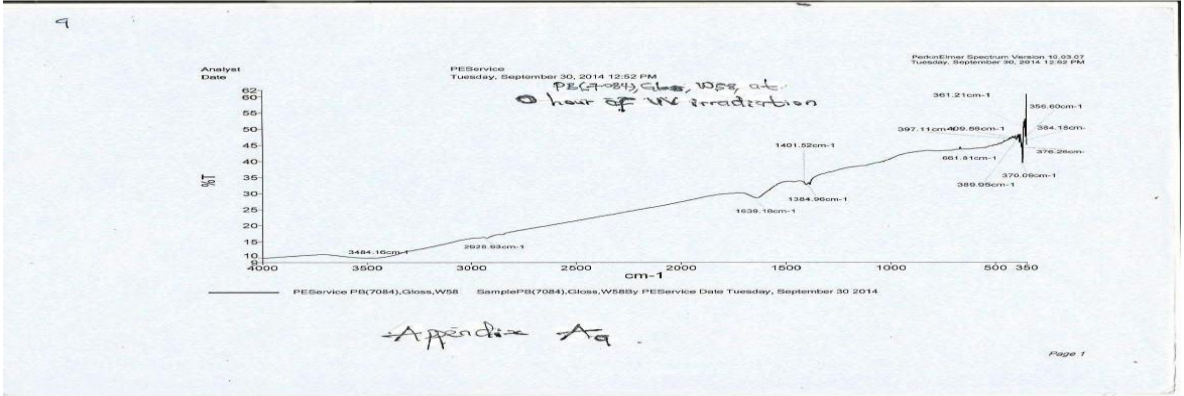


Appendix A7

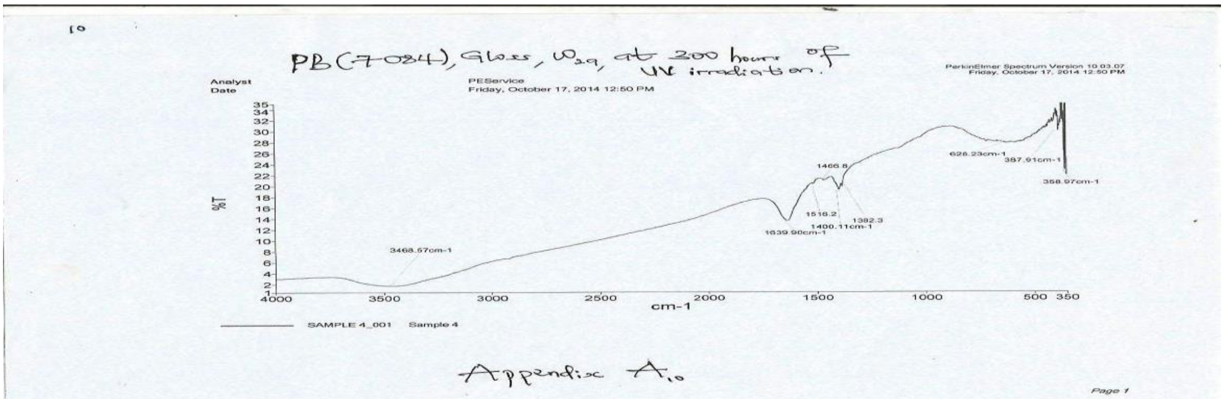


Appendix A8

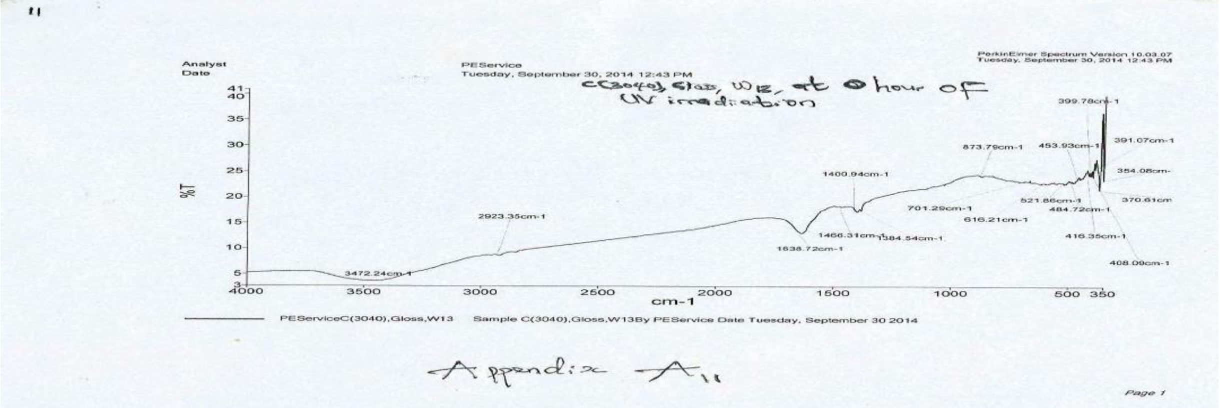
After 300 hours irradiation of BW(9102G)Gloss paint, there was a disappearance of the 2925.83cm^{-1} peak of C-H stretching of CH_3 (fatty acid) as a result of photo-degradation of drying oil binder. The O-H band also changed from a strong broad peak at 3472.47cm^{-1} to a weak broad peak around 3462.66cm^{-1}. Disappearance of 873.98cm^{-1} peak was also observed.

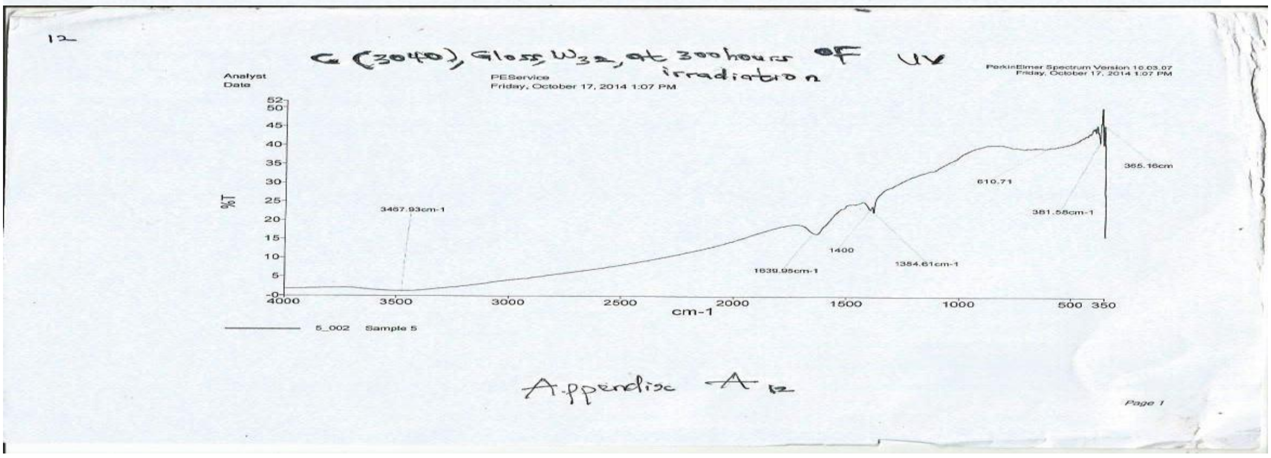


Appendix A9



Similar changes were observed for PB(7084)Gloss paint except for O-H group that changed from 3484.16 cm^{-1} to 3468.57cm^{-1}. Also, new peaks at 1516.2cm^{-1} and 1466.8 cm^{-1} were observed after 300 hours irradiation. This may be due to the formation of smaller VOCs or pigment degradation products.





The only changes observed for C(3040)Gloss paint apart from the disappearance of 2923 cm^{-1} peak, are changes in O-H peak from 3472.24 cm^{-1} to 3467.93 cm^{-1} and the disappearance of 1466.31 cm^{-1}, 873.79 cm^{-1} and 701.29 cm^{-1} peaks which may be attributed to pigment degradation.

Conclusion

All the paints examined in the current study are unstable to UV radiation and therefore undergo ageing process. Of all these Paints, Pacific Blue aged most, followed by Brilliant White while Cream is the most UV resistant. Application of varnish lacquer to nail polish helps to protect the nail polish from UV radiation as it appears to act as a UV light filter.

Acknowledgment

The authors are grateful to Prof. B.B Adeleke and the entire staff of the department of Chemistry, University of Ibadan, Oyo State, Nigeria for their tremendous and immensurable supports.

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