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Synthesis, Characterization and Antimicrobial Evaluation of Silver Nanoparticles Embedded Alkyd Resin Derived from Neem Seed Oil.

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Abstract: *Silver nanoparticles were synthesized by reducing 0.1M silver benzoate salt with 2ml of neem leaf extract, in an eco-friendly, cost effective process. Silver nanoparticles were tested to have strong zones of inhibition on the antibacterial and antifungal isolates; E. Coli, Salmonella typhi, Aspergillus flavus and mucor species used. UV-visible spectrophotometric analysis was carried out on both the silver benzoate salt and silver nanoparticles, which show bathochromic shift from 215nm (Silver benzoate) to 435nm (Silver nanoparticle). Neem seed oil was converted to alkyd resin in two steps; alcoholysis and esterification reactions respectively, and was characterized by FTIR, acid value and solubility. Antimicrobial evaluation was carried out on neem seed oil and its respective alkyd resin. Neem alkyd resin was used in the formulation of paints with percentage Pigment Volume Concentrations (%PVC) of 3 and 4% respectively, and is classified as automotive clearcoat. Chemical resistance, flexibility, light fastness, and drying schedule tests were conducted on the paints and are found to exhibit good properties which are similar to commercial paints. Antimicrobial evaluation of the paints incorporated with silver nanoparticles revealed more inhibition zones than those without silver nanoparticles.*
Keywords: *AgNP, $C_7H_5O_2Ag$, PVC%, NSO, NSOR, Paint*

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I. Introduction

Alkyd resin has since been a popular binder for surface coatings and paints formulations. However, in Nigeria today, alkyd resins are still largely imported partly due to non-availability of locally established alternative vegetable oils as raw materials. Therefore this work aims to review useful oils that are suitable as raw materials in the alkyd and paints industry in Nigeria. Vegetable oil is an important raw material for alkyd resin production. They are polyester products formed from the polymeric condensation of polyhydric alcohol, polybasic acid and monobasic fatty acids. Surface coatings such as alkyd paints and varnishes are finishes applied to the surfaces of materials to decorate and protect the surfaces (Kyenge *et al*, 2012; Odetoye *et al*, 2013).

Formulations generally have three components intended to be relatively permanent and serve specific functions in dry film. These permanent components are pigment, vehicle and additives. Pigments provide colorant or other functions. The vehicles sometimes called the binders act as the adhesive to stick pigment particles to substrate or to each other. Finally additives are chemicals that modify the properties of the coating in fluid or solid state.

Silver nanoparticles-embedded antimicrobial oil reported that, the surfaces coated with nanoparticles paint exhibited excellent antimicrobial properties by killing both the gram positive human pathogens and gram negative bacteria (Kumar *et*, 2008).

II. Materials And Methods

The reagents used were prepared using standard analytical method of preparation. Neem seed oil was purchased from National Board for Technology Incubation Centre kano, Nigeria, Neem leaf (*Azaradichta indica)* was obtained from the abundant neem trees in Bayero University Kano, Nigeria. Some of the materials used are; UV-Visible spectrophotometer, FTIR machine, Autoclave, agar plates.

Methods

Green Synthesis of the Silver Nanoparticle

Neem leaves obtained from the university surrounding were washed thoroughly with tap water followed by rinsing with distilled water and then air dried. 10g of the finely cut neem leaves were weighed and heated to boil with 100mL of distilled water, the extract is then filtered and cooled. 10mL of 1mmol $C_5H_7O_2Ag$ was then reacted with 2ml of neem leaf extract, and the colour changed slowly at room temperature overnight to golden brown.

Physico-Chemical Analysis of Neem Seed Oil with its Alkyd Resin and Characterization of Silver Nanoparticle

The physico-chemical properties such as; acid value,refractive index, iodine value,saponification number, specific gravity, percentage free fatty acid and characterization of the silver salt, silver nanoparticle through FTIR and UV-Visible analysis and FTIR characterization of the neem seed oil sample was determined in accordance with American Oil Chemists Society method (AOCS). Due to the high acid value of the neem oil as obtained from the physico-chemical analysis result (14.82), the oil will not be efficient for the synthesis of alkyd resin; hence the oil was neutralized by dissolving 4g of NaOH in 50mL of distilled water and thoroughly mixed with the oil for about 30mins. The mixture then heated to break the soap formed and was then transferred into a plastic bile for centrifugation. The new acid value was obtained after determining the normality through titration of 1NNaOH against potassium hydrogen phthalate, using the relation

$$AV = \frac{ml\ of\ KOH \times N \times 56}{gram\ \ of sample}$$

Synthesis of the Neem Alkyd Resin

Synthesis of neem alkyd resin was carried out after decolorizing the oil in two step processes; alcoholysis and esterification reactions. In the alcoholysis reaction, measured amounts of the triglycerides were placed into 1000mL of three neck round bottom flask fitted with dean and stark apparatus and heated to 120^{o}C to expel the moisture content of the oil. To this a measured quantity of glycerol and calcium carbonate (catalyst) were added and continued heating for 1hr at a temperature of 230^{o}C, until a monoglyceride forms when an aliquot of the solution dissolved completely in a methanol. In the esterification reaction, the temperature of the solution was lowered to about 180^{o}C, and the flask is connected with $N_{2,}$ to this a weighed phthalic anhydride, 10grams of xylene were added in each synthesis to aid distilling off of water of esterification by forming an azeotrope. The solution was heated for 3hrs at 240-250^{o}C and an aliquot was drawn at an interval of 30 mins to check for the drop in acid value, using the formulation in Table 1.

Table 1: Composition of Alkyd Resin Derived from Neem Seed Oil

Raw Materials	Alkyd Resin of Neem Seed Oil
Oil (g)	91.98
Pthalic anhydride (g)	48.82
Glycerol (g)	18
Oil length	57.22

Antibacterial and Antifungal Evaluation

The activity was carried out by employing paper disc diffusion method, in which the agar plates were incubated with test organisms (*E. Coli, Salmonella typhi, Aspergillus flavus, and mucor species*) by spreading uniformly. One disc from each sample was placed in the petri-dishes with sterile forceps. The dishes were incubated for 24 hours at 37^{o}C. After 24 hours, the antibacterial activity of test compound was found by measuring the zone of inhibition.

Alkyd Paints Formulation and Performance Evaluations

The paint was formulated based on pigment volume concentrations (PVC) which guides the manufacture of paint in desired properties. PVC is the concentration by volume of the pigment expressed as a percentage of the total non-volatile volume of the paints.

$$\%\ \text{PVC} = \frac{Vp}{Vp+Vb} \times 100\%$$

Where; V_p = Volume of pigment dispersion

V_b = Volume of binder.

Paint is applied on a glass slides to taste the drying through period of the paints. The dried paints each on a glass slide are immersed in to water, hydrochloric acid, and sodium hydroxide to test their chemical resistance. Scratch resistance, flexibility and light fastness were also tested.

III. Results

Table 2: UV-visible spectrophotometry of the silver benzoate salt and silver nanoparticles

Materials	**λmax (nm)**
Aqueous solution of Silver benzoate salt	215
Silver nanoparticle colloidal solution	435

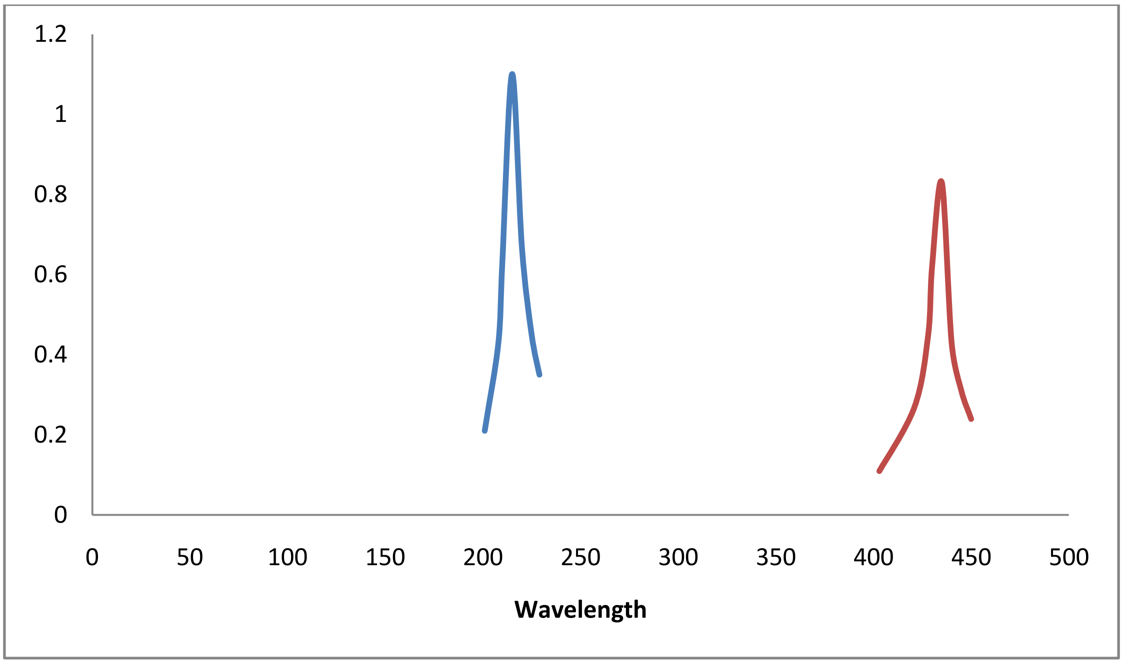

Fig1: UV-visible spectrum of silver benzoate ($C_7H_5O_2Ag$) and silver nanoparticles (AgNP)

Table 3: Physico-Chemical Properties of Neem Seed Oil (NSO).

Properties	**Neem Seed Oil**
Acid Value	14.82 (1.00912)
Iodine Value	54.8
Saponification Number (mg/g)	179.80
Refractive Index	1.458
PFFA (%)	7.41
Specific Gravity (g/cm^3)	0.9015
Viscosity (MPa at 28^oC)	90.11
Moisture Content (%)	0.47
pH	6.07

Table 4: FTIR Spectral absorption bands of NSO and NSOR

Bands (cm^{-1})	**Functional group**
3008	C- H stretch due to aromatic
2922	C-H stretch due to alkane
1745	C=O stretch due to ester
1460	C-C stretch due to aromatic ring
1110	C-O stretch due to ester
2922	C-H Stretch due to alkane
1739	C=O Stretch due to ester
1460	C-C Stretch due to aromatic ring
1164	C-O stretch due to ester
939	O-H bend due to carboxylic acid

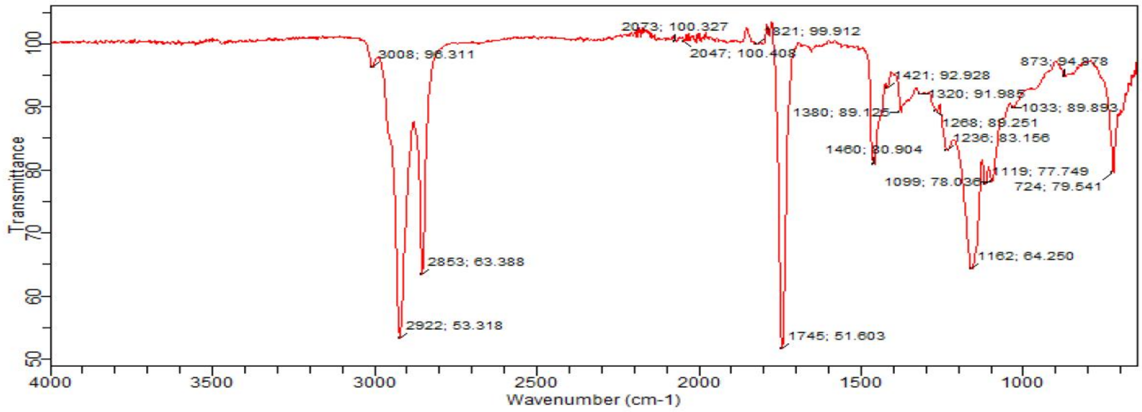

Fig2: FTIR analysis of NSO

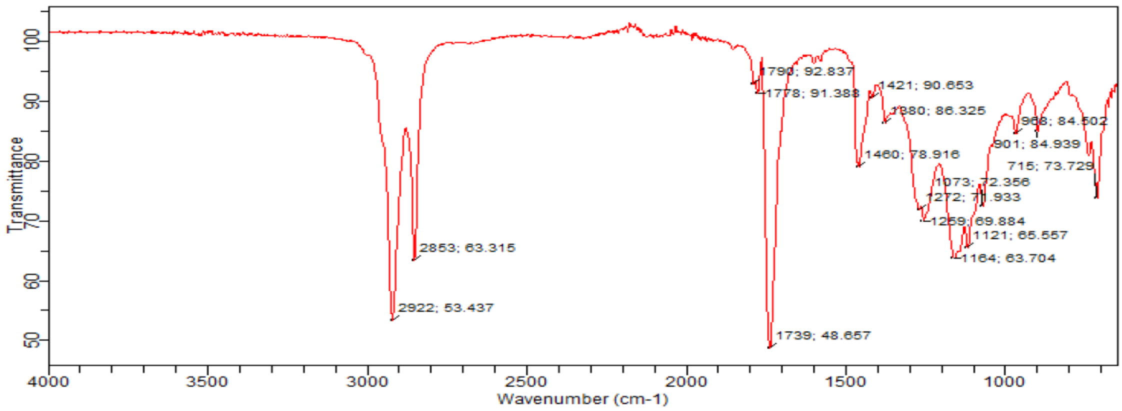

Fig3: FTIR analysis of NSOR

Table 5: Solubility of Alkyd Resin of Neem Seed Oil

Solvents	**Solubility**
Acetone	Soluble
Ethanol	Insoluble
Toluene	Soluble
Water	Insoluble
Xylene	Soluble

Table 6: Drop in Acid Values (mgKOH/g) of Alkyd Resin of Neem Seed Oil at Time Intervals

Acid Value	**Time (min)**
67.3	30
51.0	60
23.7	90
18.3	120
11.4	150
7.9	180

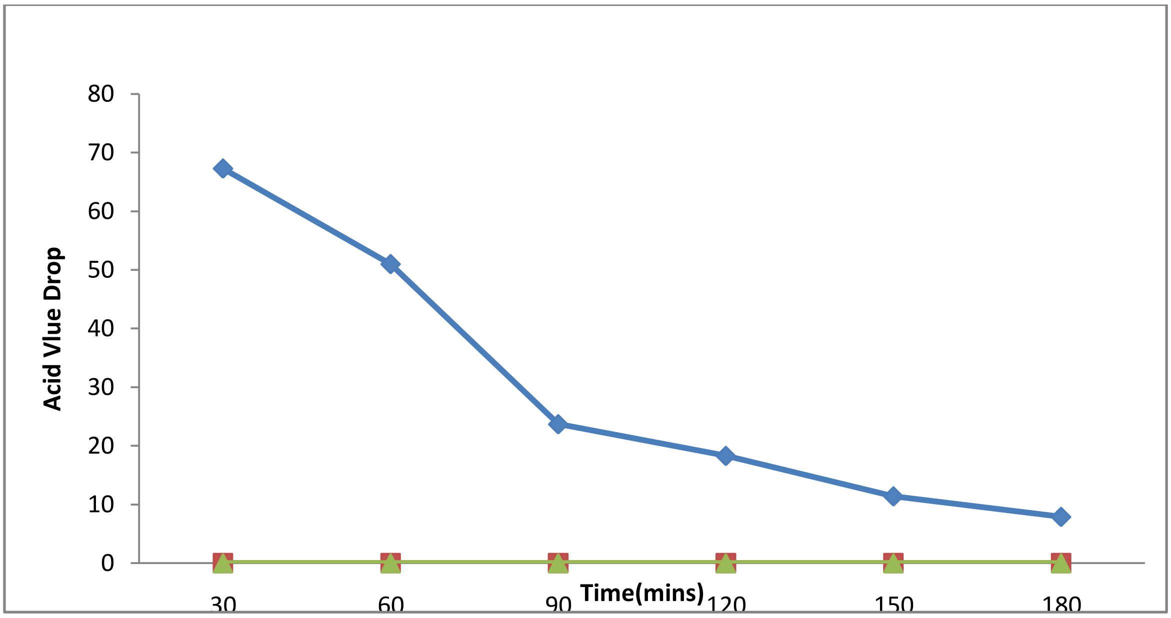

Fig 4: Graph of Acid Value Drop of NSOR

Table 7: Antibacterial and Antifungal Evaluation of $C_7H_5O_2Ag$ and AgNPs

Test organisms	Zone of inhibition (mm)/concentration (µg/ml)						Control (X)
	$1x10^3$	$2x10^3$	$3x10^3$	$1x10^3$	$2x10^3$	$3x10^3$	$3x10^3$
							Ampicilline
Eschericia coli	11	13	14	14	18	20	21
Selmonella typhi	13	14	17	18	19	21	24
							Ketoconazole
Aspergillus flavus	11	12	15	17	18	21	34
Mucor specie	10	11	12	15	18	20	25

Table 8: Antimicrobial and Antifungal Activity of NSO and NSOR

Test organism	Zone of inhibition (mm)/concentration(µg/ml)					Control
	$1x10^3$	$2x10^3$	$3x10^3$	$4x10^3$	$5x10^3$	$5x10^3$
						Ampicilline
Eschricia coli	6	6	6	6	13	21
Selmonella typhi	6	6	6	7	10	24
						Ketocon.
Aspergillus flavus	6	6	6	10	11	34
Mucor specie	6	6	7	10	11	25
						Ampicilline
Eschricia coli	6	6	6	9	12	21
Selmonella typhi	6	6	9	11	14	24
						Ketocon.
Aspergillus flavus	6	6	7	8	9	34
Mucor specie	6	6	6	8	11	25

Table 10: Composition of Alkyd Resin Neem Seed Oil Paint

Raw Materials	N_1	N_2
Resin	10	10
Pigment	7	7
Solvent	30	30
Thickner	0.2	0.2
Nanoparticle	1	0
Extender	0.4	0.4
Drier	0.1	0.1

Where;
N_1 = Paint formulation using AgNP embedded alkyd resin as binder
N_2 = Paint formulation using alkyd resin (without AgNP) as binder

Table 11: Determination of % Pigment Volume Concentration (PVC)

Components	Weight(g)		Density(g/cm^3)		Volume(cm^3)		PVC (%)	
Alkyd Resin ($N_1+Fe_2O_3/N_2+TiO_2$)	10	10	0.95	0.95	37.97	37.97	3	3
Pigments (Fe_2O_3/TiO_2)	7	7	5.242	5.242	1.34	1.34	-	-

Table 12: Performance Evaluation Tests of the Alkyd Paints

Alkyd Resin	Chemical Resistance		Flexibility Test	Drying Period	Light Fastness
N_1	NaOH	Fair	Do not crack	27:02 hrs	Excellent
	HCl	V.Good			
	Brine	V.Good			
	Water	V.Good			
N_2	NaOH	Poor	Cracks	38:07 hrs	Very Good
	HCl	Fair			
	Brine	Good			
	Water	Good			

Table 13: Antibacterial and Antifungal Evaluation of AgNP embedded Alkyd Resin Paint

Test Organisms	Zone of inhibition (mm)/concentration(µg/ml) with and without AgNP						Control
	1x10^3	2x10^3	3x10^3	1x10^3	2x10^3	3x10^3	3x10^3
Eschricia coli	6	6	6	16	17	19	Ampicillin 21
Selmonella typhi	6	6	7	19	20	21	24
Aspergillus flavus	6	6	6	17	19	20	Ketoconazole. 34
Mucor specie	6	6	6	15	18	20	25

IV. Discussions

Silver nanoparticles were synthesized by weighing 10g of the finely cut neem leaves and heated to boil with 100ml of distilled water. The extract was then filtered and cooled. 10ml of 1mmol $C_5H_7O_2Ag$ was then reacted with 2ml of the neem leaf extract, and the colour changed slowly at room temperature overnight to golden brown. The AgNP was then characterized using UV-Visible spectrophotometer. Table 2 and Figure 1 showed a bathochromic shift from 215 nm (silver benzoate) to 435 nm (AgNP). Shifting of absorption band from UV region to visible region confirmed the formation of the nanoparticle, which typically attributed to plasmon resonance of silver nanoparticles. The electron cloud at nanometer dimension can oscillate on the surface of the particles and absorb electromagnetic radiation at particular energy. The resonance developed is known as surface plasmon resonance (Behera *et al* 2015). Silver nanoparticles were synthesized according to the method described in the previous section, the colloidal solution turned pale brown, pale yellow and pale red indicating that the silver nanoparticles were formed. The UV-Visible spectroscopy revealed the formation of silver nanoparticles by exhibiting the typical surface plasmon absorption maxima at 418-420nm (Maribel *et al*, 2009).

The physico-chemical analysis result in Table 3 showed that, iodine value of neem seed oil was 54.80(cg/g), and is classified as non-drying oil. Fats and oils are made up of triglycerides molecules which are fatty acids and may be saturated or unsaturated, in other words, the number of double bonds present is normally expressed in terms of iodine value of the fat (Obibuzor *et al.*, 2014). The saponification values of the neem seed oil was 179.8(mg/g), which is the indication of the average molecular mass of fatty acid present in the oil. Saponification value of the neem oil was found to be within the range reported by (Ogunniyi *et al* 2006), and indicated that the neem seed oil contain fatty acids of high molecular weight. Acid value of neem seed oil as obtained from the result of analysis was 14.80(mgKOH/g) and it's the measure of the extent to which the constituent glycerides have been decomposed by lipase action, and has shown to be the general indication of the edibility of the oil (AOCS 1996). However, due to the high acid value of the neem seed oil, it has been refined and a new acid value of 1.00(mgKOH/g) was obtained for better alkyd resin. The refractive index of the oil was found to be 1.458. The specific gravity of the oil was 0.90(g/cm^3), which implies that it is less dense than water (Momodu *et al* 2011). Percentage free fatty acids of neem seed oil obtained was 7.41%, the viscosity of the oil at 28^{0}C was found to be 90.11Mpa, moisture content of the neem seed oil was found to be 0.47%.

FTIR spectral analysis was carried out on neem seed oil with its alkyd resin. Table 4, figures 2 and 3 shows FTIR result of neem seed oil and its respective alkyd resin with spectral absorptions of NSO at band positions; 3008 cm^{-1}, indicates C-H stretching due to aromatics, 2922 cm^{-1}, indicates C-H stretching due to alkane, 1745 cm^{-1}, indicates C=O stretching due ester, 1460cm^{-1}, indicates C-C stretching due to aromatic rings, and 1110cm^{-1}, indicates C-O stretch due to ester, while NSOR shows spectral absorptions at band positions; 2922 cm^{-1}, indicates SP^3 C-H stretching due to alkane, 1739 cm^{-1}, indicates C=O stretching due to ester, 1460 cm^{-1}, indicates C-C stretching due to aromatic ring, 1164cm^{-1} indicates C-O stretch due to ester, and 939cm^{-1} indicates O-H bend due to carboxylic acid. Results from Table 5 showed the solubility of alkyd resins of neem seed oil using various solvents, which found to be soluble in; acetone, toluene, and xylene, but insoluble in; ethanol and water. Table 6 and Figure 4 show the result of acid value drop during the formation of the alkyd resin oil with reaction time. It was found that the acid values decreases with increase in the reaction time, due to the reactivity of primary and secondary hydroxyl groups of glycerol with carboxyl groups of the phthalic anhydride as reported by (Oladipo *et al* 2013).

Table 7 shows the antibacterial and antifungal screening of $C_7H_5O_2Ag$ and AgNPs, with higher antimicrobial activity observed in silver nanoparticles than the corresponding silver salt, but in all the samples, the activity increases with increasing concentrations of silver salt and AgNPs respectively. Tables 8 and 9 showed antibacterial and antifungal properties of neem seed oil and its corresponding alkyd resin; Table 8 showed that response of organisms toward treatment at higher concentrations, with moderate activity as compared with the control (X), while at lower concentrations, the activities were lower or even zero. Table 9 showed a result with only one organism responding to treatment at all the concentrations, and showed moderate activity at higher concentration in all the organisms as compared with the control. While in some organisms, there was zero or lower activity at lower concentrations.

Table 10 shows the compositions and amounts of the components used in the formulation of alkyd paint and their respective % pigment volume concentrations (PVCs). Quantities of alkyd resins of the same seed oil were maintained in each formulation, two different types of pigments were used. In N_1 formulation, silver nanoparticle was used as an additive, and Fe_2O_3 pigment was used. While in N_2 formulation, no nanoparticle was added, and the pigment used was TiO_2. The % PVC of paints formulated are all ≤ 5%, hence the paint could be recommended for use in automotive clearcoats (Uppal, 2006).

Tables 11 showed various results for the evaluation and performance tests carried out on different alkyd paints formed. The results obtained suggests that the chemical resistance of the paints depend on the type of chemical and alkyd resin used in the formulation. The paints generally show better resistance to water and acid but poor resistance to alkali. Nanomaterials represent almost the ultimate in increasing surface area and they are chemically very active because the number of surface molecules or atoms is very large compared with the molecules or atoms in the bulk of the materials, and because of greater surface activity of nanoparticles, they can absorb more resins compare to conventional pigments and thus reduce the free space between the pigment and the resin (Mathiazhagan and Rani, 2011). Similarly, Silver nanoparticles have application in some spectrally selective coating and enhance raman scattering (Kim *et al* 2011). Scratch resistance, flexibility and light Fastness tests of the alkyd paints of N_1 and N_2 were; N_1 is more flexible than N_2, because it oxidized better and faster due to the presence of nanoparticles and pigment used, forming a strong film. The drying schedule of the alkyd paints; N_1 and N_2 were 27:02hrs, and 38:07hrs respectively. Light fastness rating of the alkyd paints N_1 and N_2 are; Excellent and very good respectively. From the result, N_1 has excellent light fastness, this is because silver nanoparticles have application in some spectrally selective coating and enhance raman scattering (Kim *et al*, 2011). Tables 12 and 13 shows the Antibacterial and Antifungal evaluations of the Neem alkyd resin paints treated with silver nanoparticles, with strong inhibition zone in the organisms of different concentrations of the silver nanoparticles, and in some organisms the zone of inhibition was even more than that of the control. Antimicrobial evaluation of the paints incorporated with silver nanoparticles revealed more inhibition zones than those without silver nanoparticles. (Sondi & Alopek, 2007) reported that the antibacterial activity of silver nanoparticles on Gram-negative bacteria was dependent on the concentration of Ag nanoparticle, and was closely associated with the formation of 'pits' in the cell wall of bacteria. Then, Ag nanoparticles accumulated in the bacterial membrane caused the permeability, resulting in cell death and they reported degradation of the membrane structure of microorganism with silver nanoparticles.

V. Conclusion

Synthesis of silver nanoparticles using an eco-friendly green synthetic method have been successfully synthesised as confirmed by UV-visible spectrophotometry. The nanoparticles were incorporated into the alkyd resin derived from Neem seed oil. The nanoparticles embedded alkyd resin was found to be active against some bacterial and fungal isolates. The resin was also used to formulate oil-based paint. The paints formulation have a % PVC range of 3-5%, hence are classified as automotive clear coats. The results obtained in this work suggest the potentiality of silver nanoparticles embedded alkyd resin derived from neem seed oil as binder in the formulation of surface coatings with enhanced antimicrobial properties and excellent light fastness.

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