Full Length Research Paper

Development of amino resins for emulsion paint formulation: effect of aldelhydic group and degree of substitution

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In our continuous effort to develop a paint binder from amino resins, amino resins from different aldehydic groups were synthesized to produce urea, formaldehyde (UF), urea acetaldehyde (UA), urea proparaldehyde (UP) and urea butaldehyde (UB) at different degree of substitution (Mono – tetra). Some physical properties of these resins were evaluated. The viscosity, gel time, density and refractive index of the resins (except UB) were found to increase with increase in alkyl length of the aldehydic group while turbidity (except UF) increased with increase in alkyl length of the aldehydic group. On the other hand, melting point and moisture uptake decreases with increase in alkyl length of the aldehydic group. In the case of the degree of substitution the viscosity, turbidity, melting point and moisture uptake increases with increase in the degree of substitution while the gel time and refractive index were found to decrease with increase in the degree of substitution. However, an initial rise followed by a gradual fall was recorded for density for the different degree of substitution for all the resins. Samples for UF and UA with the exception of monoethylol urea were too hard brittle and has low water resistance while those of UP and UB resins were too soft and remained as semi solid in the cured state at room temperature (30°C). This result indicates that these resins cannot be used alone as paint binder. However, monoethylol urea seems to have sieved itself out as a compromise candidate who is neither brittle nor too soft. A comparison of monoethylol urea with some physical properties of some convectional paint binders present it as a potential binder which may be used in the coating industry.

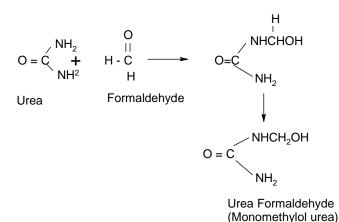**Key words:** Paint binder, aldehydic group, degree of substitution, amino resin.

INTRODUCTION

Amino resins are thermosetting polymers made by combining an aldehyde with a compound containing amino ($-NH_2$) group. However, the acceptance of amino resins as a universal material in many engineering areas such as in the coating industry is impeded by some of its inherent qualities such as brittleness, poor water resistance and formaldehyde emission (Lowel, 1990; Conner, 1996).
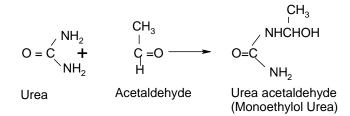
At present urea formaldehyde account for over 80% of amino resins and melamine formaldehyde accounting for most of the rest (Conner, 1996; Pizzi et al., 2001 and Updegraff, 1990). Various reports (Lowel, 1990; Conner, 1996; Achi, 2003) have shown that resins from formaldehyde aldehydic group apart from being too hard and brittle also has problem of formaldehyde emission and poor water resistance and hence it cannot be used directly as a paint binder. This has created interest in an alternative aldehydic group that can produce a resin with appropriate properties for application in a coating industry.

Teware (2000) reported that the reactivity of aldehydic groups decreases with increase in alkyl length. Mohammed et al. (2001) also reported an increase in molecular flexibility with an increase in alkyl length. However, by reacting one mole of urea with one mole of formaldehyde, acetaldehyde, proparaldehyde and butal-
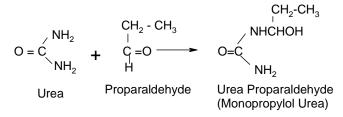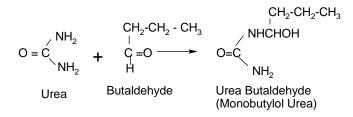
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$$O = C \overset{NH_2}{\underset{NH^2}{\big\langle}} + \overset{O}{\underset{H}{\overset{\|}{H - C}}} \longrightarrow O=C \overset{NHCHOH}{\underset{NH_2}{\big\langle}}$$

Urea   Formaldehyde

$$O = C \overset{NHCH_2OH}{\underset{NH_2}{\big\langle}}$$

Urea Formaldehyde
(Monomethylol urea)

a. Reaction of urea and formaldehyde.

$$O = C \overset{NH_2}{\underset{NH_2}{\big\langle}} + \overset{CH_3}{\underset{H}{\overset{|}{C}}} =O \longrightarrow O=C \overset{NHCHOH}{\underset{NH_2}{\big\langle}} \;\; \overset{CH_3}{|}$$

Urea   Acetaldehyde   Urea acetaldehyde
(Monoethylol Urea)

b. Reaction of urea and acetaldelyde.

$$O = C \overset{NH_2}{\underset{NH_2}{\big\langle}} + \overset{CH_2 - CH_3}{\underset{H}{\overset{|}{C}}} =O \longrightarrow O=C \overset{NHCHOH}{\underset{NH_2}{\big\langle}} \;\; \overset{CH_2\text{-}CH_3}{|}$$

Urea   Proparaldehyde   Urea Proparaldehyde
(Monopropylol Urea)

c. Reaction of urea and proparaldehyde.

$$O = C \overset{NH_2}{\underset{NH_2}{\big\langle}} + \overset{CH_2\text{-}CH_2 - CH_3}{\underset{H}{\overset{|}{C}}} =O \longrightarrow O=C \overset{NHCHOH}{\underset{NH_2}{\big\langle}} \;\; \overset{CH_2\text{-}CH_2\text{-}CH_3}{|}$$

Urea   Butaldehyde   Urea Butaldehyde
(Monobutylol Urea)

d. Reaction of urea and butaldehyde.

Figure 1. Reaction profile of different aldehydic groups with urea.

dehyde, methylol, ethylol, propylol and butylol urea resins will be produced respectively thus introducing a progressive increase in alkyl length. This increase in alkyl length may reduce brittleness and hence softness in the resulting resins.

In our previous experiment (Barminas and Osemeahon, 2007), we reported the synthesis of urea formaldehyde through a new synthetic route for the purpose of develop-

ing paint binder from amino resins which can be used for emulsion paint formulation. In furtherance to our quest, this experiment aims at synthesizing amino resins from different aldehydic groups with the objective of developing paint binder from amino resins which will satisfy the requirements of the coating industry. Reaction profile for the reactions of the different aldehydic groups with urea is given in Figure 1.

MATERIALS AND METHODS

Materials

Urea, formaldehyde, acetaldehyde, proparaldehyde, butaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were obtained from BDH.

Resin syntheses

Resin syntheses were carried out as described by Chen et al. (2001). In brief, methylol urea resins were prepared by the reaction of one mole of urea with 1, 2, 3, and 4 moles of formaldehyde to produce mono, di, tri and tetra methylol urea respectively. 0.2 g of sodium dihydrogen phosphate was used as catalyst and the pH of the solution adjusted to pH 8 by using 0.5 M H_2SO_4 and 1.0 M NaOH solutions. The solution was then heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h after which the sample was removed and kept at room temperature (30°C). For the syntheses of ethylol, propylol and butylol urea resins, the above procedure was repeated by using acetaldehyde, proparaldehyde and butaldehyde to produce ethylol urea, propylol urea and butylol urea resins respectively. The resins were analyzed at their respective gel points.

Film preparation

Films of the different resins were cast on petri dishes by using solution casting method (Mirmohseni and Hassanzadeh, 2000). The resins were then allowed to cure and set for seven days at 30°C. The physical properties of these films were investigated.

Determination of viscosity and gel time

The viscosity of the resin was evaluated outlined previously (Osemeahon and Barminas, 2006). Five different readings were taken for each sample and the average value calculated. The gel point of the different resins was determined by monitoring the viscosity of resins with time until a constant viscosity profile was obtained (Vilas et al., 2000).

Determination of density, turbidity, melting point and refractive index

The above properties were determined according to AOAC (2000). The density of the different resins were determined by taking the weight of a known volume of resin inside a density bottle using metler AT400 weighing balance. Five readings were made for each sample and average value calculated. The turbidity of resin samples were determined by using Hanna microprocessor turbidity meter model H193703. The melting point of the different film samples were determined by using Galenkamp melting point appa-
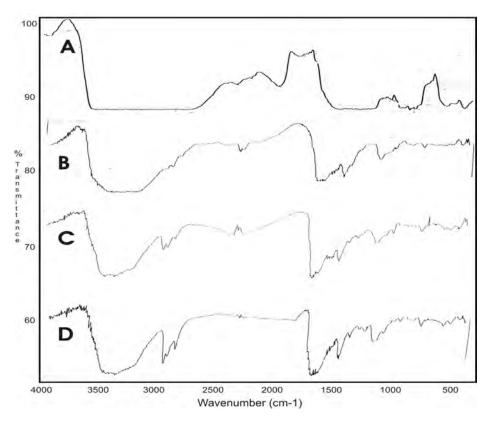
Figure 2. IR Spectra of (A) formaldehyde, (B) urea acetaldehyde (C) urea proparaldehyde and (D) urea butaldehyde.

ratus model MFB600-010F. The refractive index of resin samples were determined by using Abbe refractometer.

Determination of moisture uptake

The moisture uptake of the different resin films were determined gravimetrically (Barminas and Osemeahon, 2006). Known weight of each of the sample was introduced into a desiccator containing a saturated solution of sodium chloride. The wet weight of each sample was then monitored until maximum weight was obtained. The differences between the wet weight and dry weight of each sample were then recorded as the moisture intake by resin. Triplicate samples were used for each determination and average value recorded.

Tensile test

Tensile properties (tensile strength and elongation at brake were measured as described by Wang and Gen (2002) using instron testing machine model 1026. In brief, resin films of dimension 50 mm long, 10 mm wide and 0.15 mm thick were brought to rupture at a clamp rate of 20 mm/min and a full load of 20 kg. A number of five runs were taken for each sample and the average elongation were taken and expressed as the percentage increase in length.

Infrared (IR) spectroscopy

The IR analyses of the dried resin films were carried out by direct scanning of each film using Buck scientific 500M IR spectropho-

tometer between 600 – 4000 cm. (Barminas and Osemeahon, 2006)

RESULTS AND DISCUSSION

IR

Figure 2 shows the overlay spectra of UF, UA, UP and UB resins. In the spectra of UF, the broad band stretching from 3600 through 3100 cm^{-1} is due to O-H from UF, 2913 cm^{-1} is due to N-H, 1740 cm^{-1} is due to C=O of urea, 1557 cm^{-1} is due to N-H stretching, 1446 cm^{-1} is due to $-CH_2$ of methylene bridge and 1086 cm^{-1} due to C-O-C of ether linkage (Conner, 1996; Gan and Tan., 2000; Ahmad, et al., 2001 and Park, et al., 2001). All the above basic structural peaks of UF also appeared in the spectra of UA, UP and UB resins. This verify the fact that UF, UA, UP and UB have the same basic structure and all belongs to amino resins.

However, some little differences are observed in terms of peak heights and band shift as the alkyl length of the aldehydic group increases. Between 3500 - and 1446 cm^{-1}, the peak heights increase with increase in the alkyl length of the aldehydic group. In the case of wavelength of absorption, slight changes occurred. For example, N-H peak at 2933 cm^{-1} for UF shifted to 2943, 2968, and 2961 cm^{-1} for UA, UP and UB respectively while $-CH_2$ peak at
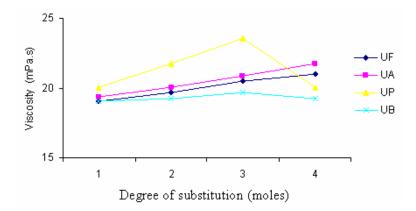
Figure 3. Effect of aldehydic group and degree of substitution on the viscosity of amino resins. UF = Formaldehyde, UA = urea acetaldehyde, UP = urea proparaldehyde and UB = urea butaldehyde.
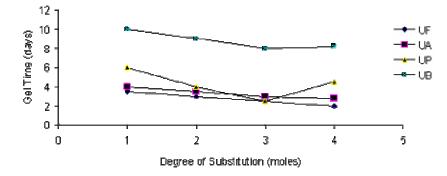

Figure 4. Effect of aldehydic group and degree of substitution on the gel time of amino resins. UF = Formaldehyde, UA = urea acetaldehyde, UP = urea proparaldehyde and UB = urea butaldehyde.

1435 cm^{-1} for UF shifted to 1446, 1455 and 1451 cm^{-1} for UA, UP and UB respectively. A careful look at these band shifts indicate an initial progressive increase in band shift with increase in alkyl length from UF- UP and then followed by a decrease at UB. This case of rise and fall implicate the possibility of crosslink dissociation at certain stage of increase in the alkyl length of the aldehydic group (Hepburn, 1982; Barminas and Osemeahon, 2006). These slight changes in terms of peak heights and band shift may affect the properties of the different amino resins. In conclusion therefore, we could verify the synthesis of amino resins of UF, UA, UP and UB by the above common structural features and their differences drawn from the increase in –CH$_2$ peak heights with increase in the alkyl length of the aldehydic group and band shifts among the different resins.

Gel time and viscosity

The processing of thermosetting resins requires understanding of the rheology and the polymerization reaction kinetics during cure (Barminas and Osemeahon, 2007).

The gel time is one of the most important kinetic characteristics of curing, because it describes the attainment of certain critical conversion responsible for the transition from liquid to solid state of the curing process (Vilas et al., 2000). The gel point is characterized by the appearance in the reactive system of a macromolecule with an infinity largely large molecular weight. The kinetic scheme of the cured paint binder is of considerable importance both from the manufacturing processes, pot stability and rate of cure of the paint film (Achi, 2003).

Rheological properties such as the viscosity and the dynamic modulus can be directly correlated to the envolving physical and mechanical properties during resin cure (Hu et al., 2001). Viscosity of a paint binder affects flow properties such as leveling and sagging (Lowel, 1990). Viscosity also affects fire resistance, drying rate of a paint film and its thermal properties (Duquesne et al., 2001). Film forming property, adhesion property and gel point of paint are also functions of viscosity.

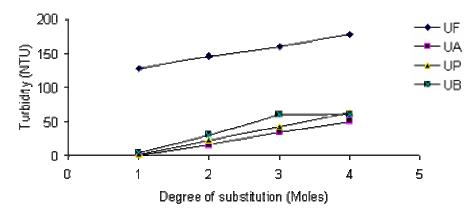Figures 3 and 4 show the effect of aldehydic group and

Figure 5. Effect of aldehydic group and degree of substitution on the turbidity of amino resins. UF = Formaldehyde, UA = urea acetaldehyde, UP = urea proparaldehyde and UB = urea butaldehyde.

degree of substitution on the viscosity and gel time of amino resins respectively. From Figure 1, it is observed that the viscosity of the amino resins with the exception of UB increases with increase in alkyl length of the amino resin. Also, the viscosity of the amino resins increases with increase in the degree of substitution with the exception of tetra UP and UB.

The above observation can be explained in terms of the differential in molecular weight and crosslink density among the different amino resins from the different aldehydic groups (Markovic et al., 2001). As the alkyl chains of the aldehydic group increases, the molecular weight also increases. However, at a critical point of tetra propylol urea, the crosslink density over short its optimal giving rise to dissociation of polymer crosslink which in turn gave rise to a more linear polymer hence the lower viscosity as observed in tetra UP and UB resins (Hepburn, 1982). The increase in viscosity with increase in the degree of substitution is in agreement with earlier report and it is due to increase in molecular weight (Ajayi et al., 2005).

From Figure 4, it can be observed that the gel time decreases with increase in alkyl length of the amino resins. This is due to the decrease in reactivity of the aldehydic group with increase in alkyl length (Tewari, 2000). The decrease in gel time with increase in the degree of substitution is attributable to the progressive increase in molecular weight (Trumbo et al., 2001). The trend observed in tetra UP and UB resins is due to dissociation of polymer crosslink which gave rise to reversion tendencies.

Turbidity

In the coating industry, the optical properties of the binder such as the turbidity are very important because it is related to the gloss properties of the paint (Trezza and Krochta, 2001). Figure 5 shows the effect of aldehydic

group and degree of substitution on the turbidity of amino resins. It is observed that UF stood out with relatively very high turbidity among the rest of the resins. At mono degree of substitution no noticeable difference exists between UA, UP and UB resins. However, as the degree of substitution increases, the turbidity with the exception of UF increases with increase in the alkyl length of the aldehydic group. All the four resins shows increase in turbidity with increase in the degree of substitution.

The increase in turbidity with increase in alkyl length of the aldehydic group and the degree of substitution can be explained interims of the differences in molecular weight which gave rise to differences in molecular morphology and orientation (Johnson and Wilkes, 2001). The behavior of UF resins is attributable to the differences in the level of crytallinity and crystalline orientation of the resin molecules (Johnson and Wilkes, 2001).

Density

In the coating industry, the density of the paint binder has a profound influence on factors such as pigment dispersion, brushability of paint, flow, leveling and sagging (Lowel, 1990). Figure 6 shows the effect of aldehydic group and degree of substitution on the density of amino resins. It is observed that with the exception of UB resin, the density increases with decrease in alkyl length of the aldehydic group. As for the degree of substitution, a trend of an initial increase in density before a gradual decrease after di degree of substitution was observed.

The increase in density with increase in alkyl length of the aldehydic group recorded in this experiment is in agreement with earlier report (Chain and Yi, 2001). It is due to the packing nature of the resin molecules (Sekaran et al., 2001; Chain and Yi, 2001). Density depends on free volume and packing efficiency of molecular chains. The reduction in density after di degree of substitution indicates inefficient molecular chain packing
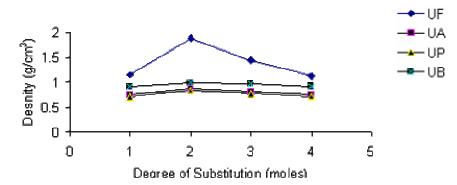
Figure 6. Effect of aldehydic group and degree of substitution on the density of amino resins. UF = Formaldehyde, UA = urea acetaldehyde, UP = urea proparaldehyde and UB = urea butaldehyde.
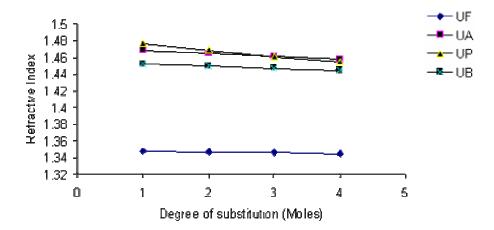

Figure 7. Effect of aldehydic group and degree of substitution on the refractive index of amino resins. UF = Formaldehyde, UA = urea acetaldehyde, UP = urea proparaldehyde and UB = urea butaldehyde.

(Chain and Yi, 2001). The initial increase in density with increase in the degree of substitution is attributable to increase in molecular weight (Ahmad et al., 2001). The behavior of UB resin may be due to crosslink dissociation which gave rise to reversion tendencies (Hepburn, 1982; Barminas and Osemeahon, 2006).

Refractive index

Gloss is an important quality factor of many coating products. The gloss of paint coating with or without pigments is a function of refractive index of the surface, the angle of incidence of the beam of light, the nature of light and the nature of the material (Trezza and Krochta, 2001). Figure 7 presents the effects of aldehydic group and the degree of substitution on the refractive index of amino resins. It can be observed that the refractive index with the exception of UB resin increases with increase in alkyl length of the aldehydic group while decreasing with increase in the degree of substitution.

The increase in refractive index with increase in alkyl length of the aldehydic group can be explained interms of increase in molecular weight (Trezza and Krochta, 2001). The decrease in refractive index with increase in the degree of substitution on the other hand may be due to differences in molecular features and molecular orientation (Trezza and Krochta, 2001; Johnson and Wilkes, 2001). The observed behavior of UB resin is again attributable to crosslink dissociation (Barminas and Osemeahon, 2006).

Melting point

The melting point of a polymer has a direct bearing to its thermal property (Bindu et al., 2001). It is related to its molecular weight, degree of crosslinking and the level of rigidity of the polymer (Park et al., 2001). In the case of the coating industry, the melting point of a binder is related to its thermal resistance as well as to its britility (Osemeahon and Barminas, 2006). The effect of aldehy-

Table 1. Effect of aldehydic group and degree of substitution on the melting point of amino resins.

Amino resin	Melting point (^{o}C)			
	Mono	Di.	Tri.	Tet.
Formaldehyde	126-128	156-158	188-200	216-218
Urea acetaldehyde	102-104	138-140	147-149	140-142
Urea proparaldehyde	ND	ND	ND	ND
Urea butaldehyde	ND	ND	ND	ND

ND: Not determined.

Table 2. Effect of aldehydic group and degree of substitution on the moisture uptake of amino resins.

Amino resin	Moisture uptake (%)			
	Mono	Di.	Tri.	Tet.
Formaldehyde	15.0	16.4	17.5	17.8
Urea acetaldehyde	6.8	7.2	7.6	7.8
Urea proparaldehyde	ND	ND	ND	ND
Urea butaldehyde	ND	ND	ND	ND

ND: Not determined.

dic group and degree of substitution is showed in Table 1. It is observed that the melting point decreases with increase in alkyl length of aldehydic group and increase with increase in the degree of substitution.

The increase in melting point with increase in the degree of substitution obtained in this work agrees with earlier report (Ajayi et al., 2005). It is due to increase in molecular weight. The decrease in melting point with increase in alkyl length of the aldehydic group can be explained in terms of increase in molecular mobility, differences in molecular feature, crystallinity and crystal-line orientation (Chain and Yi., 2001; Sekaran et al., 2001; Min et al., 2002). Thus, the softness of the amino resins increases with increase in alkyl length of the aldehydic group. Hence the existence of the cured UP and UB resins at room temperature (30°C) as semi solid obtained in this experiment is explained. This result mirror the decrease in density with increase in aldehydic group recorded in this experiment.

Moisture uptake

The interaction of structural network of polymer resins with water is both of fundamental and technical interest (Barminas and Osemeahon, 2007). Water uptake affects vital properties of the polymer material such as physical, mechanical, thermal and structural properties (Hu et al., 2001 and Nogueria et al., 2001). In the paint making industry, the moisture uptake of the binder is very crucial because it is responsible for blistering and broominess of paint film (Barminas and Osemeahon, 2006).

Table 2 shows the effect of aldehydic group and degree of substitution on the moisture uptake of amino resins. It is observed that the moisture uptake increases with increase in the degree of substitution and decrease with increase in alkyl length of the aldehydic group. The increase in water uptake with increase in the degree of substitution is attributed to the increase in OH group while the decrease in moisture uptake with increase in alkyl length of the aldehydic group may be due to the differences in chain topology which is related to the molecular size holes in the polymer structure which also depend on morphology and crosslinked density (Nogueira et al., 2001; Hu et al., 2001).

Water transport in polymer network is related to the availability of molecular-sized holes in the polymer structure and polymer-water affinity. The availability of holes depends on polymer structure, morphology, and crosslink density. The polymer-water affinity is related to the presence of hydrogen bonding sites along the poly-mer chains, which create attractive forces between the polymer and the water molecules (Nogueira et al., 2001).

Tensile test

Elongation at break determines to what extent a material stretches before breaking and hence the ductility or flexibility of the material. One of the shortcomings of urea formaldehyde resins in their cured state is that they are too hard, brittle and poor resistance to crack propagation (Lowel, 1990). In the coating industry, a paint binder must be able to exhibit some level of flexibility in order to with-

Table 3. Effect of aldehydic group and the degree of substitution on the elongation at break.

Amino resin	Elongation at break (%)			
	Mono	Di.	Tri.	Tet.
Formaldehyde	ND	ND	ND	ND
Urea acetaldehyde	125.34	60.78	ND	ND
Urea proparaldehyde	ND	ND	ND	ND
Urea butaldehyde	ND	ND	ND	ND

ND: Not determined.

stand stresses emanating from variation in environmental factors. Therefore, in developing paint binder from amino resins tensile property such as the elongation at break must be taken into consideration

The effect of aldehydic group and degree of substitution on the elongation at break of amino resins is presented in Table 3. The elongation at break of UF, UP and UB resins could not be determined because UF resins were too hard and brittle while those of UP and UB were in the form of semi solid and hence were too soft for elongation test. The tri and tetra ethylol urea resins, though softer than UF resins were also too brittle for elongation test. However, elongation at break for mono and di ethylol urea was determined and the results were 125 and 60% respectively. These observed behavior of the different resins from different aldehydic groups and those from the same aldehydic group can be explained on the basic of differentials in molecular weight, crytallinity, crystalline orientation and general molecular features (Xie et al., 2001; Chain and Yi, 2001; Wang and Gen, 2002).

Table 4 compares some physical properties of mono ethylol urea resin with films from some other convectional paint binder. The table seems to explain that the properties of monoethylol urea resin agree with those of convectional paint binders. The relatively low density of this resin is of interest and advantage as it will favor proper adhesion of binder to substrate (Gupta et al., 2001).

Conclusion

Amino resins from different aldehydic groups were synthesized to produced urea formaldehyde (UF), urea acetaldehyde (UA), urea proparaldehyde (UP) and urea butaldehyde (UB) at different degree of substitution (Mono-tetra). Some physical properties of the resins were evaluated. The viscosity, gel time, density and refractive index of the resins (except UB) were found to increase with increase in the alkyl length of the aldehydic group while turbidity of the resins (except UF) increases with increase in alkyl length of the aldehydic group. On the other hand, melting point and moisture uptake decreases with increase in alkyl length of the aldehydic group. In the

case of degree of substitution, the viscosity, turbidity, melting point and moisture uptake increases with increase in the degree of substitution while gel time and refractive index were found to decrease with increase in the degree of substitution. However, an initial rise followed by a gradual fall was recorded for density for the different degree of substitution for all the resins.

Samples from UF and UA with the exception of mono-ethylol urea were too brittle and has low water resistance while those of UP and UB resins were too soft and remained semi solids in the cured state at room temperature (30°C). This result indicates that these resins cannot be used directly as paint binder. Further research is needed in order to modify them with the aim of satisfying the requirements of the coating industry. However, monoethylol urea seems to have sieved itself out as a compromise candidate who is neither brittle nor too soft. A comparison of monoethylol urea with some properties of some convectional paint binders qualifies it as a potential binder for the coating industry.

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