

The Effect of Hydroxyl Ethyl Cellulose (HEC) and Hydrophobically –Modified Alkali Soluble Emulsions (HASE) on the properties and quality of water based paints

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Abstract

The coatings industry is a million dollar business and it is easy and inexpensive to set-up but it is growing very slowly in developing countries and this study developed a paint formulation which gives better quality and good application properties. The effect of rheology modifiers, i.e. non-ionic polymers hydrophobically-modified ethoxylated urethanes (HEUR), anionic polymers hydrophobically-modified alkali soluble emulsions (HASE) and hydroxyl ethyl cellulose (HEC) on the quality and properties of water based paints have been investigated. HEC provides the in-can viscosity and increase open working time while HASE improves application properties like spatter resistance and brush loading and HEUR provides excellent scrub resistance. Four paint recipes were prepared using four different thickeners HEC, HASE (carbopol) and Cellulose nitrate. The fourth formulation was thickened with a combination of HASE and HEC, this aimed at improving quality and at the same time reducing cost. The four samples were tested for quality tests such viscosity, sag resistance, volatile matter, tinter effect, drying times, hiding power, scrub resistance and stability on storage. Environmental factors were incorporated in the attempt to formulate an economic and green product.

Hydroxyl ethyl cellulose and cellulose nitrate gave high quality and good properties of the paint. HEC and Cellulose nitrate showed stability on storage whereas carbopol thickener was very unstable.

Keywords: Properties, thickeners, rheology modifiers, water based paints.

INTRODUCTION

Paint is essentially composed of a binder, pigment and solvent [1]. A latex paint formulation requires careful adjustment of the rheology. The interaction or association between the ingredients of a typical paint formulation cannot be ignored in order to develop coating rheology systems [2]. A latex paint requires the addition of thickeners to achieve the desired rheological behaviour [3]-[7]. These rheology modifiers may be synthetic non-ionic polymers like hydrophobically-modified ethoxylated urethanes type (HEUR) and anionic polymers like polyacrylic acids or hydrophobically-modified alkali-swelling/soluble emulsions (HASE) [8]. The important features of rheology are highlighted by the methods of application; roller/brush loading, open working time, hiding power, spatter resistance, flow and levelling effect [9]-[11]. Hydroxyl Ethyl Cellulose (HEC) was for many years the main and only thickener used in water based paints. It provides the in-can viscosity. Application properties like sag resistance are controlled by the HEC. It also helps to increase the open time [12].

The use of HEUR (Hydrophobically-modified ethoxylated polyurethane) rheology modifiers is a patented technology but it has the disadvantage that HEUR polymers are insoluble in water and thus their use must be accompanied by use of surfactants, which complicates their application, increase the ingredients of the formulation and result in high price of paint. HASE polymers offer ease of dosing, excellent viscosity building, wide formulation latitude, excellent biostability, and are supplied as high solids latex, free of organic co-solvents. The thickening properties of the HASE polymers are developed on swelling in the presence of water, alkali or an organic base [13]. The coatings industry is a multi-billion dollar business and it is easy and inexpensive to set-up but it is growing very slowly in developing countries which still need structural developments. According to our survey most paint manufacturing companies are not manufacturing due unavailability of raw materials because of economic decline. Some companies import paint in bulk and repackage it as they find it is cheaper to do so than to manufacture their own. In this paper we report a new paint formulation which is very economic for developing countries and of significantly better quality.

EXPERIMENTAL

A. *Procedures for Preparation of the Paints*

A mixing vessel was cleaned and ingredients were weighed according to the master formula.

1) Preparation of Sample 1

Water, SHMP 001 and HEC were added to the vessel and mixed for 5 minutes under low speed (400 - 700 rpm). Ammonia (5 %), Alcospere, Antifoam, Nipacide and NP9 were added separately in this respective order and allowed to mix for 2 - 3 minutes under low speed (400 – 700 rpm). Tioxide, Kulu 10, Kulu5 and snow-white were added separately in this order and mixed under high speed (1000 -1400 rpm) for 20 – 25 minutes until fog was 50 µm maximum. A minimum quantity of water was added to clean the walls of the vessel. Water, Texanol, MEG and Antifoam were added orderly and mixed for 10 minutes under medium to high speed (700 – 1000 rpm) ensuring that temperature is kept below 40 °C. LDM was added and the mixture was mixed at low speed (400 – 700 rpm) for 15 minutes. Aqua and Alcolgom were added and the final mixture was mixed for 10 minutes at high speed (1000 - 1400rpm).Ammonia was added in small amounts until a desired viscosity was achieved.

2) Preparation of Sample 2

For sample 2 a mass of (0.0316 kg) carbopol a HASE polymer was used instead of HEC and the procedure was performed exactly the same way using the same equipment and operating conditions.

3) Preparation of Sample 3

Water, SHMP 001, (0.0158 kg) HEC and (0.0133 kg) HASE were added to the vessel and mixed for 5 minutes under low speed (400 - 700 rpm). Ammonia (5 %), Alcospere, Antifoam, Nipacide and NP9 were added separately in this respective order and allowed to mix for 2 - 3 minutes under low speed (400 – 700 rpm). Tioxide, Kulu 10, Kulu5 and snow-white were added separately in this order and mixed under high speed (1000 -1400rpm) for 20 – 25 minutes until fog was 50 um maximum. A minimum quantity of water was added to clean the walls of the vessel. Water, Texanol, MEG, and Antifoam were added orderly and mixed for 10 minutes under medium to high speed (700 -1000rpm) ensuring that temperature is kept below 40 °C. LDM was added and the mixture was mixed at low speed (400 – 700 rpm) for 15 minutes. Aqua, Alcolgom and ammonia were added and the final mixture was mixed for 10 minutes at high speed (1000 – 1400 rpm).

4) Preparation of Sample 4

Water, SHMP 001 and 0.0133 kg Cellulose nitrate were added to the vessel and mixed for 5 minutes under LSD 400-700 rpm. Ammonia (5 %), Alcospere, Antifoam, Nipacide and NP9 were added separately in this respective order and allowed to mix for 2 - 3 minutes under low speed (400 – 700rpm). Tioxide, Kulu 10, Kulu5 and snow-white were added separately in this order and mixed under high speed (1000 - 1400 rpm) for 20 – 25 minutes until fog was 50 µm maximum. A minimum quantity of water was added to clean the walls of the vessel. Water, glycerin , MEG and Antifoam were added orderly and mixed for 10 minutes under medium to high speed (700 -1000rpm) ensuring that temperature is kept below 400 °C. LDM was added and the mixture was mixed at low speed (400 – 700 rpm) for 15 minutes. Aqua, alcolgom

and ammonia were added and the final mixture was mixed for 10 minutes at high speed (1000 -1400 rpm) until a uniform smooth emulsion was formed.

B. Tests methods

The paint samples were allowed to cool overnight and laboratory samples were collected for analysis the following day. The following tests were performed;

1) Viscosity

Viscosity was measured twice during the production process using different types of viscometers.

a) Brookfield Viscometer

This viscometer was used to determine the viscosity of water solutions i.e. the paste prepared from the thickeners.

b) Stormer Viscometer

The Stormer Viscometer was used to determine the viscosity for the final product. This is also known as application viscosity. The paint sample was cooled to 25 ± 2 °C. The sample was poured into the stainless steel cup and filled to 10 mm of the container lip. The sample container was placed directly on the can adapter mounted on the viscometer base. The desired display (KU or gm.) was selected using the display unit selector switch. The viscometer lifting handle was moved down to the lowest position. This automatically immersed the spindle into the fluid up to the immersion mark of the spindle. After waiting for some few seconds the value was directly read out as the KU value and the associated gram value (gm.) was also displayed at the same.

2) Sag Resistance

The paint was applied to a chart with anti-sag meter graduated from 3 – 12 ml. The chart was placed immediately in a vertical position with the thinnest stripe at the top and left to dry. The reading was read directly from the anti-sag meter.

3) Drying Time of a Paint Film [16]

The films are allowed to dry in a horizontal position in a drying room with a temperature of 25 ± 2 °C and a relative humidity of $50 \pm 5\%$ under light from fluorescent daylight type lamps. The film was tested at points not less than 20 mm away from the edge. Two parameters were determined.

a) Surface Dry

Sand was sprinkled from a height of 150 mm on to the film and left there for 1 minute. The sand was then removed by gentle brushing with the camel hair brush. The surface was observed for injuries to the film.

b) Hard Dry

The panel was placed in a horizontal position on the balance and place a piece of cloth, approximately 25 mm square, on the panel. The cloth was held downwards with the ball of the thumb until the specified mass was indicated by the balance. Maintaining the pressure the thumb and cloth were turned at an angle of 90° in the

plane of the panel. The film was examined for loosening, detachment, wrinkling or other evidence of distortion of the film. Determinations were made at half to two hour intervals depending on the speed of drying of the film.

4) Determination of Wet Hiding Power/ Opacity [17]

The mass per litre of the well stirred paint was determined. A convenient quantity of the paint was decanted into a 500 ml container. The brush was dipped into the well-mixed paint and worked out on a clean surface. Then the brush was laid flat over the top of the container and the mass of the container plus paint, plus brush, was weighed to the nearest 0.1 g. The paint was applied to the test area of the chart, taking care that no paint is lost between the container and the test area. The paint was brushed out evenly over the test area, adding more or removing the paint, until the background was just completely obscured, until the black and white areas were no longer discerned through the paint film. The test surface was observed immediately after each fresh application or removal of paint. Viewing was done under a reasonable intensity of diffused daylight (light from the southern sky) in a direction normal to the surface of the chart, with the daylight striking the test surface at about 45°. When the black and white pattern of the chart was just completely obliterated, the mass of the container plus brush was re-determined and the amount of paint used was calculated.

5) Fineness of Grind [18]

A Grind gauge was used to perform this test. The correct Gauge was selected in order that the pigment size is within the scale of the gauge, such that the highest precision is obtained in the determination of fineness of grind of the sample. The gauge, was placed the deepest end of the path/s furthest away, on a flat, horizontal, non-slip surface, and the surface of the gauge was wiped scraper blade edge was cleaned with a lint free cloth. The prepared test sample was thoroughly stirred in order to achieve even distribution of pigment. Sufficient quantity of the sample was poured onto the deep end of the gauge, sufficient to just overflow the channel/s. The scraper was held using the thumbs and fingers of both hands in a vertical position. It was placed perpendicular on the gauge surface, at the edge of the deep end, ensuring a right angle between the face of the scraper and the length of groove/s path. Sufficient downward pressure was applied to clean excess sample from the gauge face. The gauge was viewed from the side, such that the line of vision is at a right angle to the path/s of the drawdown. The angle of the gauge was adjusted, so to make the line of vision from the light source appear in the sample material of the gauge. The position along the path/s of the gauge where the first indication of a speckled par tem occurs, opposite isolated specks prior to this position was observed. The fineness reading was read directly from the scale opposite the particle distribution.

6) Scrub Resistance/Wet Abrasion

A Wet abrasion scrub tester was used. The abrasion head holder was put up; and two fastening frames were took out and put down to the prepared test panel on the glass plate. The test panel was fixed horizontally using fasten frames with painted side up. The brush which has been pre-treated was put into the abrasion head holder and kept

to drop naturally. Approximately 2 ml washing liquid was dropped on the test area of the panel. The pump power source was plugged into the socket on the side of the machine. Liquid solutions were pumped to the brush heads from the detachable container mounted to the side of the tester. The machine began to work and it counted automatically the number of cycles to remove one continuous thin line of paint film across the 12.7 mm width of the shim. Two of the drawdowns were tested and if the results were different by more than 30 % of the average, the third drawdown was then tested.

7) Volatile Matter [19], [20]

The drying dish and the glass rod were dried in an oven for 30 min at 105 °C, and cooled in a desiccator and weighed together to the nearest 0,01 g. 4,5 g of paint were accurately weighed into the dish and then heated for 3 hours in the oven with the temperature maintained at 105 °C. During the drying period, the stirrer was used at intervals to break up any skin that may have formed. The sample was then cooled in a desiccator and weighed accurately to 0,01 g.

8) pH

The pH meter was calibrated by inserting the electrode into a pH 6.86 (25 °C) buffer solution. The setting screw was adjusted with special tool until the displayed value was equal to the pH value of buffer solution at that temperature. The electrode was then inserted into a pH 4 (25 °C) buffer solution. The slope screw was adjusted with special tool until the displayed value was equal to the pH value of buffer solution at that temperature. The electrode was then rinsed with distilled water and inserted into the sample to be measured. The pH value was displayed on the meter and recorded.

9) Tinter Effect

A sample mass of 500 g was decanted into a separate beaker and 25 g of the tint was added and the sample was mixed accurately and allowed to stand. The viscosity of the sample was then read at 25 °C and any deviation noted.

10) Colour Acceptance/ Rubout Test

A tinter of a desired colour was added to the paint and then the paint was applied to a white chart. A rub-out test was performed after drying. The chart was rubbed out for 30 seconds, the paint was judged for color differences.

11) Storage Stability

The samples were kept for 4 weeks at 48 °C in a stability cabinet and the above tests were repeated and any deviations from the initial results were noted.

RESULTS AND DISCUSSION

The essential quality control tests such as viscosity, volatile matter, pH, drying time, sag resistance, stability on storage, colour acceptance and tinter effect were analysed in each of the four samples prepared. The effect of different types of thickeners was

assessed. The results obtained were compared to those of a formulation employed in industry with HEUR used as a thickener. The standards used in these experiments were from the Standard Association of Zimbabwe [16], [17]. All samples appeared to be good and satisfying the specification that they should be uniform, shiny and free from lumps. Samples 1, 3 and 4 matched the standard except for Sample 2 which appeared to be slightly different from the standard.

Fig. 1 shows and compares the viscosities of all the paint samples, the standard had a viscosity which is within the specification. It dropped slightly upon tinting and after 4 weeks storage. Sample **1** was thickened by Hydroxyl ethyl cellulose, the final viscosity of the paint sample was 122 KU which is within the limits after tinting it dropped slightly to 118 KU. The viscosity did not drop upon storage however it was accompanied by a slight drop in the sag resistance. Sample **2** thickened with carbopol had a final viscosity of 115 KU after tinting a great drop of the viscosity down to 92 KU was observed. It further dropped to 85 KU upon storage. Sample 3 thickened with a mixture of HEC and Carbopol had a final viscosity of 113 KU, the viscosity dropped to 106 KU but did not drop further upon storage. The resistance to tinter effect was brought by the contribution of HEC within the sample components. Sample **4** was thickened with Cellulose Nitrate. It had a final viscosity of 129 KU which dropped to 121 KU after tinting. The viscosity kept on increasing upon storage showing a greater power of overcoming tinter attack. This showed that cellulose nitrate and alcogum form a good combination in maintaining the rheology of the paint.

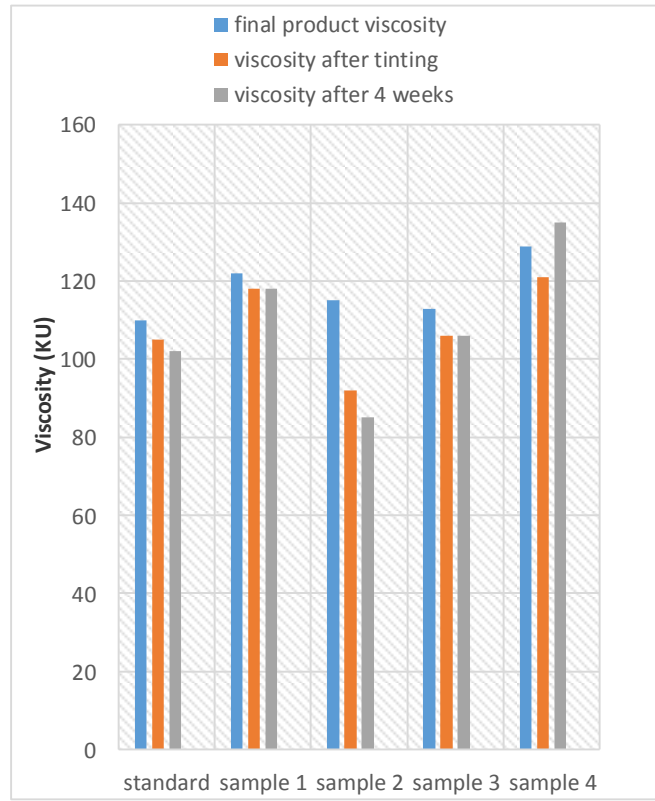


Figure 1. Comparison of Viscosities of all the samples

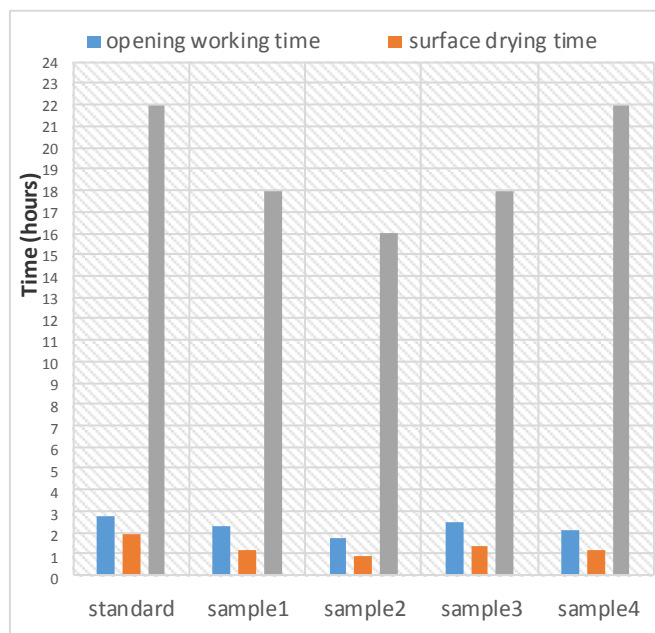


Figure 2. Drying times of all the samples

The universal tinter used is observed to be having a negative effect on the final viscosity of the paint. This is because of the incompatibility of the composition of the paint and that of the tinter. The universal tinters are composed of Chromophoric Pigment, Extender Pigment, Water Ethylene Glycol, Octyl Phenol Ethoxylate, Phosphate Ester Surfactants, Polycarboxylate Dispersant and Soya Lecithin (a drying oil). Looking closer to the paint formulation comparing with the tinter composition the mis-matching components are the Phosphate Ester surfactants. Studies looking at the contributions of the individual components in universal colorants identified the largest contributor to KU drop as the Phosphate Ester surfactant present in universal colorants. This surfactant interacts with the associative thickener network by disrupting the thickener adsorption onto latex and lessening the self-association between certain thickeners [14].

Investigation of various types of HASE thickeners showed that viscosity changes with universal colorants can be minimized through proper combination with a cellulose thickener as observed with Sample 3. The liquid form HASE thickener worked well compared to the powder form Carbopol. Universal tinters works well with thickeners of larger particle size ($> 200 \mu\text{m}$) but does not perform well in smaller particle size ($< 124 \mu\text{m}$) [14]. From the data sheet Carbopol 934P used has a particle size between 3 - 7 microns. This small particle size is the reason why there was great viscosity drop of 23 KU. Sample 4 thickened with cellulose nitrate gave results of interest which had a different trend compared to the other samples. The final viscosity was within the limit it dropped to 121 KU but still within the limit. On storage the viscosity kept on increasing, after 4 weeks accelerated time the viscosity was found to be 135 KU. This can have a positive and negative impact to final user of the paint. This is an advantage to the painter as the viscosity can be reduced by thinning with water thereby increasing the quantity of the paint. However this requires a skilled painter because this process will compromise on the binder and weakens the strength of the paint. If over thinned the paint will show low water resistance and the colour adhesion on the surface will be affected indicated by the colour fading faster. 4 weeks accelerated time (in a stability cabinet) is equivalent to 6 month real time. This means Sample 4 cannot have a shelf life of more than six months. The problem of viscosity drop for Sample 1; 3 and 4 can be corrected by slightly over thickening the paint so that after tinting the viscosities drops to values within the specified limits. However this adds extra cost to the formulation. Sample 2 may be improved by choosing a better grade of carbopol with a larger particle size.

The pH values of all the samples were within the specified range. The pH of the final product should remain constant to prevent fouling of the paint. Ammonia is used to adjust the pH during the manufacturing process. The effectiveness depends on the initial pH of the water to be used, and that of the aqueous dispersion. Problem were encountered with Carbopol thickener, the aqueous dispersion had a pH of 2.5 this consumed a lot of ammonia to adjust the pH to 7.5. The pH is adjusted to above 7.5 so as to ionize dispersants. If the pigments, extenders are not optimally dispersed in the water properties such as low opacity, low sheen, poor tinter acceptance and poor sag

resistance are observed. Thus Sample 2 gave a low sag resistance value and had a pH value of 7.20. Sample 1 and the standard shows that the sag resistance is related to the pH but Sample 4 shows some uniqueness it had a pH of 8.20 but sag resistance of 14 less than of Sample 1 with a lower pH this because the pH of aqueous dispersion of Sample 4 had a pH of 5.1 so the dispersant was not fully ionized to control the sagging of paint however it is resistant to sagging upon storage.

Sample 2 failed the test for wet scrubbing as it gave a number of cycles less than the specified limit. Scrub resistance is related to film thickness the thicker the film the more resistance it is against erosion. Film thickness depends on the amount of volatile matter and viscosity of the paint. Sample 2 had a lower viscosity and also because of its small particle size the effectiveness of the binder was reduced causing this sample to adhere less strongly to the surfaces. Sample 4 shows a greater resistance to scrubbing because it has a higher viscosity, therefore forms a thicker film on application and also has a low amount for volatile matter. The standard gave a greater resistance to scrubbing even though it had a higher amount of volatile matter because the HEUR is insoluble in water and therefore difficult to wash away with water but flakes away after some time. Sample 3 shows a lower resistance compared to sample 1 this is because of the contribution of the carbopol in the sample.

The standard drying time should not be 4 more than 4 hours but should be optimum to allow open working times so as to make some corrections but not very highly to inconvenience the user. Sample 1; 3 and 4 gave reasonable drying times and also for both surface and hard drying times. Sample 2 dried very quickly showing some skinning and cracks. This was because of improper dispersion of the extenders within the thickener. In this experiment the drying time was difficult to determine because of changing weather conditions. Drying times should be determined at 25 °C and 50 % relative humidity.

Hiding power of paint measures the ability to obscure a background of a contrasting colour. A good paint formulation should have as low contrast ratio as possible so that a less paint is required to obscure the background. Good dispersion of pigment in the binder media strongly influences the hiding power of the. Pigment particles agglomeration reduces the hiding power efficiency of the pigment. Low hiding power in a paint can be caused by inefficient de-agglomeration and pigment flocculation. Titanium dioxide is the widely used pigment used in water based paints. The main characteristics of TiO₂ that influence hiding power are high refractive index and optimized particle size [15]. Sample 1, 3 and 4 show good hiding power however Sample 2 shows a poor hiding power because of the small particle size of the carbopol powder compared to that of the pigment.

The colour acceptance is also affected by particle size of the thickener. Poor dispersion in a wrong thickener causes colour instability and therefore fades away quickly. On performing the rub-out test colour differences were observed for Sample 2. Sample 1, 3 and 4 gave no colour differences showing good thickener colour

compatibility. Fineness of grind is to determine the degree of dispersions in the aqueous thickener media. Dispersion agents are added to the mixer just after the thickener and grinded for about ten minutes then a grind gauge is used to measure the fineness of grind. It should be not 10 μ m if more than that the grinding is continued to achieve a small particle size. The standard and Sample **1** gave a fineness of 5 μ m thus they gave a good dispersion. Carbopol gave fineness of 7 μ m it was difficult and it required more time to be grinded and dissolved in water. Sample **4** gave a fineness of 8 μ m maybe this is because since cellulose nitrate has a larger particle size, grinding for ten minutes was not enough to produce finer particles. However this did not affect the other properties of the final paint.

A. Environmental Considerations

EMA has put some regulations to the paint manufacturing industries since paints contain organic compounds and heavy metals. The formulations used in this research contain Titanium which is a light metal and no studies have proven its carcinogenicity. However the formulations have 20 – 38 % volatile matter. We made efforts to reduce the amount of organics by replacing the coalescing agent Texanol with glycerine plant origin in Sample **4** hence a lower percentage of volatile matter was obtained. Texanol is Propanoic acid, 2-methyl-, monoester with 2, 2, 4-trimethyl-1, 3-pentanediol. The glycerine was observed not have a negative impact on the properties of the paint. The standard thickened with HEUR had a higher value of the volatile matter than cellulose derivatives, and this formulation has been proven to have negatives effects on the environment therefore should not be thrown down the water drainage system. Cellulose derivatives are environmental friendly and are biodegradable.

B. Economic Considerations

- 1) Cost Comparison for Different Paint Ingredients

Table I: Price Comparison for Some Paint Ingredients

Thickener	Country of origin	Price per unit kilogram	Landing cost in Bulawayo
HEC	China	\$1.42	\$ 12.35
HEUR	Germany	\$13.13	\$24 .10
Cellulose nitrate	China	\$1.08	\$10.93
Carbopol	USA	\$0.59	\$8.42
Texanol	USA	\$6.85	\$19.46
Glycerine	Zimbabwe	\$0.70	\$0.86

*Prices as at February 2015

The thickener is the main component of a paint formulation and the final price of the paint depends on the price of the thickener. The HEUR thickener is expensive and it is exported from Germany and this results in higher price of the paint in Zimbabwe. Hydroxyl ethyl cellulose and nitro cellulose are cheap and originally from China, however freight and duty charges makes the price of the paint become high. Carbopol is a synthetic polymer originally from the United States of America it is cheap and the freight and duty charges are reasonable however it gave a poor quality of paint. Glycerine from Zimbabwe is cheaper and environmentally safe gave good quality and better properties of the paint. Therefore glycerine can safely replace Texanol as a coalescing agent. Comparing the cost of the formulations the standard is the most expensive to manufacture. Sample 1 would be more expensive than sample 2, 3 and 4. Sample 4 would be the cheapest to produce the price of the glycerine would reduce the final cost by more than half. Sample 2 is cheap but not recommended to produce due to poor properties.

CONCLUSION

Based on our studies it has been observed that the thickener used influences the quality and properties of the paint. In particular there is a clear indication that the use of cellulose derived thickeners can reduce the manufacturing cost in African industries resulting in lower prices of the paint and the thickeners are environmentally friendly since they are biodegradable. Properties such viscosity drop and poor sag resistances were observed after 4 weeks storage. However blending the thickeners (HEC+ Carbopol) improved properties to above those of carbopol. The Carbopol thickener gave a shorter drying but resulting in skinning and cracking. From observations of all the parameters analyzed in this study, it can be concluded that HEC and Cellulose nitrate can substitute HEUR thickener in water based paints. The aim of this study was to investigate the effect of HASES and HEC on the quality and properties of water based paints hence we conclude that the both quality and properties depend on the type and grade of the thickener. Cellulose nitrate showed very good thickening efficacy and gave good properties to the final product. The formulation with cellulose nitrate as a thickener and glycerine as a coalescing agent can be employed and implemented by local paint manufacturing industries. However, cellulose nitrate should be handled with care because it is explosive.

We are currently furthering our studies to optimize the existing formulations so as to meet fast growing demands and to improve the manufacturing processes with technological aspects.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to Astra Paints Bulawayo, Zimbabwe where most of the experimental work was carried out.

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