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E. I. DU PONT DE NEMOURS & COMPANY

FABRICS & FINISHES DEPARTMENT

CHEMICAL DIVISION

PARLIN LABORATORY

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PROJECT J-1047

SUBJECT: ACCELERATORS FOR FURNITURE "DULUX"

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INTRODUCTION

The setting up or hardening of Furniture "DULUX" is accelerated by acids. The rate and extent of setup as well as the compatibility and stability vary with different acids. Mineral acids are generally not desirable because of poor compatibility with the "DULUX" solution as well as their deteriorating effect on the substrate used. Several years ago a "butyl acid phosphate" was developed which accelerated the set-up and still was compatible. Later an "octyl acid phosphate" was found to give a faster and more complete setup to the "DULUX" film as well as to effect a better rubbed clarity and print resistance than was previously obtained with the "butyl acid phosphate."

The purpose of this work was to investigate the possibility of preparing an accelerator which had even better properties than "octyl acid phosphate." Another purpose was to endeavor to learn the mechanism of the reaction between the "DULUX" and the accelerator.

SUMMARY

Several alkyl acid phosphates have been prepared with alcohols from ethanol (C_2) to dodecanol (C_{12}) in place of the 2-ethylhexanol (C_8) now used. The phosphorous pentoxide content was varied above and below that used in the current formulation. These experimental alkyl acid phosphates were evaluated as accelerators for Furniture "DULUX". Evaluation on walnut panels has shown that when the same molar ratio of alcohol to phosphorous pentoxide is used there appears to be little or no effect caused by varying the alcohols. A variance of the amount of phosphorous pentoxide used with a given alcohol showed that as the phosphorous pentoxide was reduced below that currently used a softer film is produced and when the amount of phosphorous pentoxide is increased a hard film with slightly poorer cold crack resistance is formed. The accelerator with the higher amount of the pentoxide appears to have somewhat poorer stability. It is concluded that the present octyl acid phosphate accelerator formulation (C-174) gives the optimum cure from the standpoint of rubbed clarity and cold crack resistance and has about the best composition for stability.

PATENT SITUATION

Octyl acid phosphate is covered by U.S. Patent 2,274,447 assigned to the Reichhold Chemical Company. The duPont Company has been granted a free license for the preparation and use of this composition. The work carried out under this project has produced nothing patentable in light of previous patents in the field.

EXPERIMENTAL

The rate of cure or hardening of ureaformaldehyde resins, such as those used in Furniture "DULUX" can be greatly accelerated by the addition of an acid. Because of the several disadvantages of mineral acids, such as incompatibility and corrosion, a butyl acid phosphate composition was used for some time. U.S. Patent 2,274,447 (Reichhold) disclosed an octyl acid phosphate composition which was also found to accelerate this cure rate. Evaluation studies showed the latter material to give a more rapid cure, and a better all-around finish. Previous work here was directed only toward the development of the process for the preparation of the octyl acid phosphate. The work under this project has been directed at investigating other alkyl acid phosphates in the search for a better accelerator than the one now in use and to endeavor to learn something of the mechanism of the reaction involved.

The complex nature of the product limited the analysis to the determination of acid number, non-volatile content and color. The acid number was determined by titrating a weighed sample of the material in neutral alcohol with standard aqueous sodium hydroxide solution. All of the solids determinations in this report were determined by placing a weighed sample of the material in a shallow glass dish in an air circulating oven at 105°C. for four hours and noting loss in weight. (More recent work at the Oldbury Electro-Chemical Company laboratory indicate that a non-circulating oven gives more consistent results). All color comparisons were made with the Perlin scale.

The early work on the preparation of octyl acid phosphate indicated that if the temperature of the reaction was allowed to rise very much above 40°C. the product would separate into two layers. Therefore in this work cooling baths were provided at all times to prevent the temperature of this exothermic reaction from rising too high.

In the course of the present work several alcohols have been investigated in place of the 2-ethylhexanol in the present octyl acid phosphate formulation (C-174). This C-174 formulation also contains a small amount of ethyl Cellosolve and n-butanol. The various alcohols were used to replace the 2-ethylhexanol on an equal mole basis, so that the weight of alcohol varied considerably from the lowest to the highest molecular weight alcohol used. However, it was felt that this would give a fairer comparison of the alcohols since the functionality was always the same.

The amount of non-volatile material after the reaction varies somewhat from batch to batch and also with the molecular weight of the alcohol, so that all of the accelerators were diluted to 50% non-volatile material with toluene. Representative runs with different alcohols are tabulated in Table I.

It is readily seen that as the molecular weight of the alcohol increases, the acid number of the accelerator at 50% solids decreases. The last item in this table (n-butyldihydrogen phosphate) was included for academic reasons as a material whose exact composition is known. The sample designated 2216-133 is a laboratory batch of standard C-174 accelerator.

The amount of phosphorus pentoxide used with a given alcohol was also varied to learn the minimum amount which would give satisfactory cure. The phosphorus pentoxide was also increased in order to discover the maximum amount that could be incorporated into the formulation and to determine whether the cure time could be shortened or the bake temperature lowered. Table II shows the composition of the accelerator when the amount of phosphorus pentoxide was varied while keeping the amount of n-octanol constant. No more than 150 g. of P_2O_5 could be incorporated into the reaction mixtures.

A typical laboratory experiment (2216-163) will be described. To a 1 liter, three neck flask equipped with an anchor stirrer and a thermometer is added 100 g. of toluene, 9 g. of (ethyl) Cellosolve and 100 g. of n-octanol. To this is added 100 g. of phosphorous pentoxide in small portions over the period of about two hours. A stopper is kept in the unused neck of the flask except at such times as additions are made. As the reaction is extremely exothermic an ice bath is raised around the flask from time to time in order to keep the temperature below 35°C. It has been found that the P_2O_5 is best weighed quickly and then stored in a desiccator over P_2O_5 between additions. After all of the P_2O_5 has been added the mixture is stirred for one hour and then 16 g. of n-butanol is added slowly. The final mixture is allowed to stir for an additional hour before being sampled for analysis. If the non-volatile content was found to be over 50% sufficient toluene was added with stirring to bring it down to 50% ± 2%.

EVALUATION

The octyl acid phosphate accelerator is used by adding 5% solid accelerator to the Furniture "DULUX" based on the solid ureaformaldehyde resin in the "DULUX". This amounts to 2 parts of the accelerator solution to 98 parts of "DULUX" (RK-5760). Therefore all evaluations were carried out with these amounts. It was found to be very difficult to pick up small differences in performance of the various accelerators when pours of the RK-5760 accelerator solutions were baked on glass panels. Therefore samples of accelerators which were considered as representative of the point being considered were evaluated following the standard procedure on walnut veneer panels. The panels are treated as follows: (a) sanded, (b) was coated with 19380 Sealer, scuffed, (c) filled with 27-5017, air-dried overnight (d) sealed with 19380, dried (e) a 2 mil topcoat applied - one half of the panel being sprayed with the RK-5760 - C-174 control and the other half with RK-5760 plus the experimental accelerator. The panels are then air-dried for one hour and finally baked for two hours at 120°F. At the

same time pours of the topcoats are made on glass and the time for the film to become tack free is noted. After the films have been baked, the panels are allowed to cool and are then processed by sanding and buffing. The panels are rated on their rubbed clarity, i.e. freedom of haze and degree of polish, and on print resistance. This latter test is made by applying 2 and 4 pounds per square inch to a piece of duck cloth placed on the film overnight. The amount of printing of the weave of cloth on the finish is compared to the standard. The results obtained with the accelerator evaluated are given in Table III.

From this table it can be seen that when the standard amount of P_2O_5 is used there is very little difference in effectiveness of the accelerator although the alcohol is changed from C4 to C12. The rubbed clarity of panels increases as the amount of P_2O_5 used with a given alcohol is increased while the cold crack resistance falls off. This is to be expected since a harder film will take a better polish but it is more brittle and hence has poorer cold crack resistance. It is also seen that n-butyldihydrogen phosphate and phosphoric acid will cure the film although not as well as the alkyl acid phosphate accelerators.

It has been shown that the addition of 2 to 4% of water to the RK-5760 accelerator solution will cause it to gel in from 1 to 7 days at elevated temperatures, e.g. 120°F. However, films prepared from these solutions containing additional water before they have set up do not show any improved or degenerated properties. Trialkyl and triaryl phosphates will not cure the RK-5760 on baking.

MODE OF ACTION

The method of action of these alkyl acid phosphate accelerators is not understood. Because of the complexity of the two solutions involved it is felt that a study of the reaction is beyond the scope of this work. However, it is now thought that the role of the acid number of the accelerator is minor. Table I shows the acid numbers of the alkyl acid phosphate accelerators varying from 159 to 280 and yet apparently there was little difference in the effectiveness of any of them. And while the n-butyldihydrogen phosphate with an acid number of 716 cures the film, it is not as good as the alkyl acid phosphates. Further work along this line is not contemplated at this time.

TABLE I

Designation	Alcohol	After Reaction		After Dilution			Remarks
		Acid No.	Solids	Acid No.	Color	Solids	
2216-125	Ethanol	280	62.9	242	9	50.3	No Cellosolve used
2216-130	n-Butanol	238	66.6	174	35	48.5	only n-Butanol used
2216-158	n-Hexanol	226	67.3	169	500 +	51.4	
2216-133	2-Ethylhexanol	199	60.5	170	500 +	47.3	
2216-163	n-Octanol	211	70.4	153	125	50.8	
2216-161	n-Decanol	204	72.8	140	100	50.4	
2216-162	n-Dodecanol	159	73.0	127	500 +	51.0	
2216-200	n-Butyldihydrogen phosphate	716	100	not diluted			

TABLE II

Designation	g. P_2O_5	Acid No.	% Solids	Remarks
2216-193	20	76	24.8	
2216-194	35	135	42.8	
2216-189	50	174	55.0	
2216-172	75	212	69.6	
2216-163	100	211	70.4	This represents the Std. amount of P_2O_5
2216-186	100	200	72.8	Only n-octanol used
2216-173	125	235	73.8	
2216-190	150	233	75.7	Stable for only a short time

TABLE III

Accelerator Designation	Alcohol Used	Parts of (a) P_2O_5	Rubbed Clarity	Overnight Printing 2#	Overnight Printing 4#	Cold Crack
C-174	2-Ethyl-hexanol	100	8	9	8	8
2216-204	n-Butanol	50	5	7-	5+	
2216-130	n-Butanol	100	8+	8+	7+	8
2216-193	n-Octanol	20	5		5+	
2216-189	n-Octanol	50	6		6	9+
2216-163	n-Octanol	100	8	9+	8	8
2216-173	n-Octanol	125	9		9	6+
2216-190	n-Octanol	150	9		8+	6+
2216-211	n-Dodecanol	50	5	6+	4+	
2216-162	n-Dodecanol	100	8	9	7+	8
2216-212	n-Dodecanol	150	7+	8	7	7+
2216-200	n- Butyl dihydrogen phosphate		7	9-	7+	
	Phosphoric acid (b)		6	7	6	

(a) 100 parts P_2O_5 is standard

(b) 3.75% based on U-F

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