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UNION CARBIDE AND CARBON CORPORATION
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Resins for Solution Coatings

Beer Can Lining Project - Summary

A frank discussion of the evaluation of the initial sample of vinyl chloride-vinyl benzoate copolymer has been held with representatives of Stoner-Mudge, Inc. It was made clear that, in spite of very distinct advantages shown by this resin over the competing "Geon" 200 x 20 vinyl chloride-vinylidene chloride material, it will be necessary to market the CZ-L copolymer at 40-45¢ a pound to be attractive for the beer can coating business.

While the economics of producing this type of resin are being studied, work is being concentrated on development of less-costly substitutes with satisfactory properties. The 3,3,5-trimethylcyclohexanol derivatives continue to show most promise. Optimum compositions for the copolymers of vinyl chloride with the maleate ester now seem to be more clearly defined, and resins containing the acrylate ester are being examined as rapidly as possible. Development-scale runs of some of these are planned for the near future, and should yield valuable information on the ultimate worth of the resins.

Vinyl Chloride-Vinyl Benzoate Copolymers

Stoner-Mudge, Inc., of Pittsburgh, have completed evaluation of the toluene-soluble vinyl chloride-vinyl benzoate resin (CZ-L) submitted to them recently, and have reported their findings to Corporation representatives in a conference held in Pittsburgh on November 16. Their tests of this resin tended to confirm the findings of this laboratory, and it is their opinion that beer can coatings based on the material would have merit. They are especially attracted by the heat stability, filterability, and ability to get good adhesion to commercial can primers by blending in small quantities of resin VAGH; in all of these properties resin CZ-L is superior to resin "Geon" 200 x 20. However, 200 x 20 permits slightly higher solids in the thinners which Stoner would use, and the CZ-L resin would have to sell at prices equivalent to or lower than that of 200 x 20 to be attractive. Therefore, while the cost angle is being studied, closer attention is being paid to the trimethylcyclohexanol esters, as discussed in other sections of this report.

A supply of CZ resin blends is being built up from autoclave runs made by the Development Department. Many of these have been high in viscosity, however, and it is hoped that this will be corrected before much resin is accumulated. In general, CZ-L resin appears to be quite attractive for coatings uses, and it is possible that this higher-viscosity material would be of interest in these other outlets. A sample of CZ-24, in which the reduced viscosity in m.i.b.k. was 0.496 (as compared with the 0.40-0.45 figures for CZ-L) was sent to Mellon Institute for evaluation along these lines.

Three samples of laboratory-size batches were received for study for a possible patent memorandum. They were as follows:

Resin	Cl/Benz. Charge	% Conversion	% VCl	Red. Visc. (Cyclo.)
69-BT-64	57/43	15.8	69.3	0.51
69-BT-65	44.5/55.5	13.0	54.8	0.42
69-BT-68	44.5/55.5	20.8	59.2	0.44

All three resins were toluene-soluble and had good blush and impact resistance. The solution of 69-BT-64 in toluene was slightly viscous, but there were few other differences.

Vinyl Chloride-Di(3,3,5-Trimethylcyclohexyl)Maleate Copolymer

With a swing away from CZ resin as a beer can coating appearing to be a possibility, this type of copolymer seems to be one of the leading substitutes. It has been demonstrated in two recent samples, 69-BT-46 and 69-BT-71, that good toluene solubility, coupled with good blush and impact resistance, are characteristic of these resins when the proper compositions are realized. The exact optimum has not yet been determined, for the first of the above samples contained 62.8% vinyl chloride with 0.37 reduced viscosity, while the second one contained 67.2% vinyl chloride with 0.40 reduced viscosity. Something close to the latter is probably what is desired, especially since the higher vinyl chloride content would make the cost of the finished resin lower. However, with the anticipation that larger-scale work with these maleates will be desirable, tests of other properties have been begun with the resins at hand, notably compatibility, solubility, print point, and other essentials.

Vinyl Chloride-3,3,5-Trimethylcyclohexyl Acrylate Copolymer

Three samples of these resins have been received, but only one has been examined thoroughly for can coatings, so far. All were charged at 95/5 chloride-acrylate ratio, but were carried to different conversions. The first resin, 69-BT-76, at 24.8% conversion, was reported to contain 80.9% vinyl chloride, with a reduced viscosity of 0.48 (cyclohexanone). Blush and impact resistance were good, but solutions required 50% methyl isobutyl ketone to be usable and were quite viscous, even then. The other two resins are being evaluated at this time, but no results are available, beyond solubility, which

does not seem too encouraging, still. The very great disparity in polymerization rates between vinyl chloride and the acrylate ester (the ester being much the faster) makes the preparation of uniform copolymers quite difficult on small scale. Arrangements are under way to produce such copolymers in a small autoclave where better control of monomer feed can be realized.

Vinyl Chloride-3,3,5-Trimethylcyclohexyl Crotonate Resin

Potentially, this could be a very good alternate to the CZ type of resin as a beer can coating, for several samples have shown highly desirable properties. Costwise, it is judged that the crotonate resin should be superior to the maleate analogue, because it should permit more vinyl chloride in the copolymer at optimum compositions. Unfortunately, the crotonate copolymer is none too easily polymerized, and prospects are not very bright. The latest batch, resin 69-BT-41, was made from a 57/43 chloride-crotonate charge carried to 3.85% conversion, ending with 72.5% vinyl chloride and a reduced viscosity of 0.42. It gave viscous solutions in toluene and had poor blush and impact resistance. It is not thought that the sample is very representative, but since polymerization of this type of resin is very slow and difficult, the outlook for extensive investigation is not very encouraging.

Vinyl Chloride-Di(2,4-Dichlorophenyl "Cellosolve") Maleate Resin

It had been hoped from the initial batch of this resin that good can coating properties might be realized by adjustment of the monomer ratio and the molecular weight. From the two samples examined this month, it does not appear as though this will be possible. Vinyl chloride content was dropped to 70% and reduced viscosity to 0.41; toluene solubility was not gained, and films were brittle. Further work with this sort of copolymer seems unprofitable.

High-Pressure Copolymers

Several resins made by high-pressure reactions have been received for evaluation. One of these, a vinyl chloride-ethylene copolymer, 7-W-96-A (or 69-BT-69), with 79.7% vinyl chloride and 0.56 reduced viscosity (cyclohexanone), has been examined. The general properties, with the exception of blush resistance, look interesting. Poor resistance to hot water was noted, but this should not be characteristic of such copolymers, and further investigation is planned. Meantime, some vinyl chloride-isobutylene copolymers have been received, and work is being started with these.

Resin VAGH

The viscosity control problem which stemmed from the sodium methylate catalyzed process for producing resin VAGH appears to have been overcome successfully by the plant, at least for the current run, by selection of higher-molecular weight starting resin. In actual production, this will be a help to the

Production Department, for the use of VYHH resin with higher specific viscosity will make precipitation and recovery somewhat easier.

However, a complaint from Stoner-Mudge, Inc., which was referred to this group, has focussed attention on some actual and some possible shortcomings of resin VAGH. One of these troubles arises from the yellow color which is characteristic of new-process material. The Production Department plans to counter this by occasional runs make by the old methanolic sulfuric acid process. However, another difficulty involves loss of adhesion of a specialized coating containing resin VAGH combined with urea-formaldehyde and epon resins. The causes of the trouble have not yet been located, but the problem is being investigated jointly by the local, Mellon Institute, and customer's laboratories. A separate memorandum on the subject has been issued.

Resins for Suspensions

Chlorotrifluoroethylene (Fluorothene Resin)

Principal effort is being directed toward finding a method of eliminating the mud-cracking tendencies of coatings applied from organosols of the suspension polymerized CF3 resins. Addition of 20 to 40% CFE wax, on the weight of dry resin, is showing some promise but as the wax is more expensive than the resin a better method is needed. A possible method is a long high bake; in one case a smooth glossy coating of suspension polymerized resin on steel was obtained after a bake of 17 hours at 273°C. Incidentally, adhesion over the base steel was very good and the coating was tough and not degraded.

In making hydrosols, water dispersions of the suspension resins, it was found that there is an optimum amount of n-butanol in the water for maximum fluidity. This was 5 to 10%. Cast films still cracked badly. It was found that a CFE wax emulsion could be made and then blended with the hydrosol but crack-free films have not been obtained yet.

The material for preparing a quart of wash primer was sent to Westinghouse for test as a primer in fiberglass laminates. Further tests on fiberglass laminates are being made here. An organosol of bulk resin in toluene allowed too much evaporation of thinner, and a coating on fiberglass cloth cracked and did not fuse well. However, an organosol of 20% resin in 75/25 Solvesso 150/toluene allowed a coating of 150% resin on the cloth weight to be applied in one coat with no sagging, cracking, or blistering. This formula will be passed on to Westinghouse.

One sample of "presumably maleic acid modified" chlorotrifluoroethylen resin, 68-BT-642 was examined for possible improved adhesion to steel. Such a resin is being considered as a can coating resin because of high heat stability and good water and chemical resistance. However, this sample gave a very brittle coating, as formed from a hot melt of the powder on a panel, and so it is considered of no further interest. Its molecular weight appeared to be too low. It was easily soluble in hot durene.

Vinyl Chloride-Acrylonitrile (Resin NYGV)

This project is waiting for the "Vinyon" N Resin Unit to produce resin of larger ultimate particle size. Then an effort will be made to produce another batch or two of organosol grade resin. Also, a higher hardening temperature than the 70°C. formerly used will be tried in an effort to improve recovery of the resin.

Three samples of regular production "Vinyon" N resin from run C21-327, representing hardening temperatures of 120°C., 115°C., and 110°C., were evaluated for use in organosols. Surprisingly, they wet down well at 50% resin in the standard 50-50 xylene-isophorone thinner, but after grinding they became thicker and eventually had to be reduced to 40% resin content. All gave fairly good cast films. The film baked at 110°C. was best, but even after 48 hours grinding there was too much cloudiness in the films due to undispersed agglomerates. Thus, even 110°C. hardening temperature is too high.

Resin Latices

The possibilities of cross-linking consecutively-polymerized butadiene -- styrene-acrylonitrile resin latices to produce solvent-resistant films were explored in a preliminary way this month. While some films were as high as 87% insoluble in boiling cyclohexanone, accelators and thermosetting resin combinations tried thus far were ineffective in increasing the insolubility over that obtained by simple heating. These partially thermoset films have excellent flexibility and reasonably good water resistance; further work to improve solvent resistance at lower baking temperatures is being undertaken.

Electrodeposition of Resin Powders

This project was relatively inactive this month. Attempts were made to coprecipitate vinyl chloride latex and vinyl acetate latex to produce a powdered resin with a "pressure sensitive" adhesion surface. The particular dispersion systems tried were incompatible, hence special compatible systems will have to be made to evaluate this method of densifying the powdered resin film.

Electrophoresis of Organosols

This project has been reactivated, utilizing a circuit based on the Cenco electronic electrometer, which was unavailable when electrophoresis was last undertaken. One of the principal difficulties of a mechanical nature connected with electrophoresis of organosols is the extremely low current (10^{-13} ampheres) which must be measured. This has been largely overcome by the use of precision resistors of very high value, used in parallel with the very sensitive electrometer. Experimental work will begin shortly.

Convertible Coatings Vehicles

A copolymer of styrene and allyl "Cellosolve" acrylate was made to check a patent claim. This polymer had most, if not all, the chemical and physical properties desired in a food can lining resin. Furthermore, the polymerization of this potentially three-dimensional resin was carried to high conversion without any sign of gel formation. The reason for this interesting and important behavior is being investigated. Since the dilution, temperature and catalyst concentration did not seem to be enough to account for the formation of soluble polymer, a study of the monomer pair was started. Preliminary results indicated that the particular combination of monomers was necessary to avoid gelation. Replacement of some of the styrene with ethyl acrylate caused gelation at lower conversion.

A review was made of the hydrolysis of vinyl chloride-allylidene diacetate copolymers. This represents one approach to the preparation of aldehyde-containing resins. Acid hydrolysis yielded an uninteresting mixture of resin components, some of which were soluble in acetone while others were soluble only in cyclohexanone. In an attempt to avoid this, hydrolysis was carried out with 90% of the theoretical amount of potassium hydroxide. Although analyses are not available, a change in resin properties shows that reaction was effected rapidly and without discoloration. The resin so obtained was soluble in methyl isobutyl ketone and could be insolubilized somewhat by heating even though the theoretically possible number of aldehyde groups was low. Subsequent study of the hydrolysis and of resin properties will be carried out on copolymers containing more allylidene diacetate.

A few efforts have been made to cross-link copolymers of ethylene and allyl acetoacetate. These resins contain about 35% of the reactive monomer and judging from the fluidity of toluene solutions have a low molecular weight. In the granular or film form they are soft, waxy and weak. It is felt that very efficient cross-linking will be necessary to convert the film to hard, strong materials.

Plasticizers

Plasticizers for Vinyl Chloride-Acrylonitrile

A second series consisting of twenty compounds was briefly evaluated as plasticizers for NYGL resin (same as Vinyon N but lower molecular weight). Most were incompatible with the resin and showed cloudiness, sweatout, or imparted no flexibility. However, two look promising. They are butyl dibutyl-phosphonoethyl sulphone and nitrilotris-(beta-propionitrile).

Paint Industry Show

The Coatings Division was represented at the Bakelite exhibit at the annual Paint Industry Show, held this year in Chicago in conjunction with the meeting of the Federation of Paint and Varnish Production Clubs. Wile various

technical problems were discussed with a number of different customers and prospects, questions of resin supply were of paramount interest. It was quite evident that the vinyl resin coatings have become well known in the industry from the types of questions which were asked.

The "bubbling" problem in resin VYNV.2 plastisols for slush molding was reviewed in considerable detail with representatives of Stanley Chemical Company. This seems to be related to the water soluble material being left on the resin by the present production process, and the plant plans to try to minimize this as soon as convenient. Stanley also reported favorably upon their development work with resin NYGV organosols.

Among the other exhibitors there were several things of particular interest to us. Some alkyd producers talked of new alkyds which are reportedly compatible with resin VAGn. Several suppliers listed vinyl resin stabilizers and plasticizers. Shell stressed their new epoxide type ("Epon") resins for coatings uses.

Sales Meeting

The first half of this year's divided sales meeting of the Coatings and Adhesives Materials Division of Bakelite was held in Chicago in advance of the Paint Show. Data on plasticizer evaluation in plastisols and on the surface replica electron micrographs of organosol films were presented to the field men. A portion of the meeting of the Thermosetting Department's Varnish Resin Division was attended also.

American Can Project

It is proposed to submit to the American Can Company black iron panels coated with a baked vinyl resin finish which will withstand food can processing cycles of up to an hour at 250°F. This is the first step in assisting them in their efforts to find suitable coatings for tin-less cans. It has been necessary to have the steam processing kettle repaired so as to withstand the necessary pressure, and this has delayed this work. These repairs have been completed now.

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