

BUSINESS CONFIDENTIAL

MONTHLY REPORT

MEMORANDUM

RECEIVED

OCT 15 1968

R. N. Wheeler

TO: Dr. C. K. Fink

FROM: W. H. Bauer

DATE: October 1, 1968

SUBJECT: Vinyl Resins and Plasticizer Summary - Tarrytown Technical Center
September, 1968

CALENDERING, FLOORING AND RECORDS

VINYL SUSPENSION RESINS FOR CALENDERING (333 S 90)

1. HAARTZ AUTO FABRICS, ACTON, MASSACHUSETTS

A Technical Service call was made at this company in an attempt to define some of the formulating variables which were contributing to die-lip hang-up in the dry blend extrusion of vinyl coated cloth. The problem was reportedly more severe with the use of BAKELITE® resin QSAP-7 than with Geon 102 EP F5. It was established that "plate-out" tests, which are considered useful for predicting calender and embossing roll plate-out, did not correlate with the die-lip build up experienced at Haartz. The customer will explore the effect of lubricants and pigment dispersing aids, but overall dry blending and extrusion performance characteristics indicate that Geon 102 EP F5 is favored over QSAP-7. This is consistent with our laboratory evaluations of Geon and BAKELITE dry blend grade resins.

(L. G. Krauskopf)

2. VINYL CHLORIDE - ETHYLENE COPOLYMERS

Results of thermal stability studies on vinyl chloride - ethylene copolymers have been discussed with the Business Team. The following course of action has been adopted:

- a) Phase II, a study of plasticizer response of these copolymers, will be carried out, and
- b) Stabilization studies will be conducted concurrently utilizing Ba-Cd-Zn systems and epoxy plasticizer.

UCC
070090

Target date for next review is the first week in November.

(J. A. Young)

PLASTICIZERS FOR CALENDERING (333 S 50)

1. ROSS AND ROBERTS, STRATFORD, CONNECTICUT

A Technical Service call was made at this company for consultation purposes on various formulations for calendered flexible vinyl film and sheeting, which have demonstrated erratic failures under low temperature impact. In addition to formulating variables, it appears that Ross and Roberts maintains insufficient control over their calendering procedures.

(L. G. Krauskopf)

2. FLEXOL EPO

Accelerated compatibility tests continue on laboratory prepared samples containing epoxidized soybean oil as the sole plasticizer. After two months, both the Paraplex G-62 and FLEXOL EPO plasticized samples continue to show good compatibility.

(L. G. Krauskopf)

3. FIELDS PLASTICS AND CHEMICALS CO., LODI, N. J.

Plastisol viscosity data is in the process of being generated for John Dickson to combat a plasticizer change by Fields Plastics and Chemicals Co. The change has been to diisononyl phthalate (DINP) from FLEXOL DIOP because of better volatility properties. Two blends of FLEXOL DIOP and FLEXOL 10-10 are being considered to compete with DINP. The two blends will be better or equivalent to DINP in volatility properties.

(T. A. Grillo)

4. PLASTIC CALENDERING CORP., FARMINGDALE, N.Y.

At the request of Mr. R. A. Hornack of our Clifton Sales Office, a formulation based on FLEXOL 10-10 and EP-8 was suggested to meet Mil spec LP-375 b.

(E. B. Harris)

FLOORING PLASTICIZERS (333 R 50)

1. EFFICIENCY COMPARISON - BUTYL BENZYL PHTHALATE
VS. FLEXOL 128 IN DIDP BLENDS

Because of the discrepancy found in comparative efficiency data for pure FLEXOL 128, BBP and blends of the two with DIDP, an additional study of these systems was made. It appeared that efficiencies of these esters in blends with DIDP were not additive functions of composition as is usually true. Therefore, blends of DIDP with BBP and blends of DIDP with FLEXOL 128 were prepared at 0, 25, 50, 75 and 100% DIDP. Vinyl asbestos tiles were prepared from these blends at 25, 30 and 35 PHR. Hardnesses (McBurney indentation) were determined for these stocks and curves developed representing hardnesses as a function of % DIDP in the blend at constant PHR levels. In all cases, both BBP and FLEXOL 128 exhibited maxima in these hardness vs composition plots. This finding explains the increased difference in efficiency between BBP and FLEXOL 128 when DIDP blends are used. It also serves as a basic consideration to be explored in future new plasticizer evaluations.

(R. P. Braddicks)

2. WATER SENSITIVITY - BBP AND FLEXOL 128 IN VINYL
ASBESTOS TILE

Vinyl asbestos tile producers have been and still are critically concerned about water sensitivity of their product. Detailed comparison of BBP and FLEXOL 128 affect upon water sensitivity of tile has been completed. Interpretation of data generated in this study indicates that in almost every case BBP is slightly better than FLEXOL 128 regarding its contribution to this property but in no case does FLEXOL 128 exhibit sufficient failure to warrant its rejection. This study included expansion properties resulting from immersion of tile in water, softening of tile due to immersion in water, as well as softening due to exposures of samples to 100% R.H. Comparison was made with stocks containing Canadian Asbestos as well as stocks made with Calidria (Coalinga) asbestos.

(R. P. Braddicks)

FLOORING, ASBESTOS APPLICATIONS (333 R 80)1. TINCTORIAL STRENGTH OF TITANATED SG 100 IN VINYL ASBESTOS TILE

Two grades of titanated SG 100 asbestos were compared with untreated SG 100 with conventional mode of pigmentation in vinyl asbestos tile. Both SG 100-20 and SG100-35 were both colorimetrically and visually rated as white pigment savers in this application. Discussion of this work with marketing personnel (N.J. Setter and L. D. Harris) resulted in the decision to further explore this concept. Tile grade white TiO₂ pigment R 101 will be employed instead of the R 992 used in this study. This investigation will also aim at determining if an optimum level of white pigment for admixture with SG 100 exists. It is hoped that such a mixture will offer greatest customer appeal and thereby enhance sales of SG 100. Carbide's economics of producing this product will be critically assessed since sales of asbestos and not white pigment is desired.

(R. P. Braddicks)

PLASTICIZERS FOR WIRE AND CABLE (223 T 50)1. FLEXOL 1023

Insulation resistance measurements on vinyl insulation containing FLEXOL 1023 were found to be one-seventh that of FLEXOL 13-13 using a laboratory prepared sample of the new plasticizer. Subsequent I R measurement on insulation using material from the first plant-run of FLEXOL 1023 showed it to be one-half that of FLEXOL 13-13. Volume resistivity of 1023 by the 13-13 specification procedure shows that it meets 13-13 specifications. Since it is the general opinion of Operations Team 84 that the electrical properties of the plasticizer cannot be improved, one more measurement of insulation resistance will be made on freshly prepared wire insulation. Multiple measurements will provide confidence in the differences in performance, if they be real.

(E. B. Harris)

MOLDING AND EXTRUSIONPLASTICIZERS FOR MOLDING AND EXTRUSION (211 V 50)1. ENDICOTT-JOHNSON, JOHNSON CITY, N. Y.

This company purchases approximately 17 MM pounds/year of granular vinyl compound (not UCC's) for injection molded shoe soles of various types. They have decided to manufacture their own compound on old rubber processing equipment.

First attempts have been rather unsuccessful, primarily due to lack of formulating knowledge. The desirable effect of a number of formulating variables was demonstrated in a day of plant trials. It appears that UCC will gain a significant share of the vinyl resin and plasticizer business when Endicott-Johnson's operation gets going.

(L. G. Krauskopf)

2. THERMOPLASTIC PROCESSES, INC., STIRLING, N.J.

Work has been initiated on a sample of plasticized vinyl from Thermo-plastic Processes Inc. The work involves physical property testing of a proposed tubing compound as an independent testing laboratory.

(T. A. Grillo)

SPECIAL PROJECTS

PLASTICIZERS, EPOXY, MISCELLANEOUS PROCESS STUDIES (446 F 30)

1. FLEXOL EPO COMPATIBILITY

a) At the request of the Oxidation Products Operations Team, the importance of the FLEXOL EPO specification values on iodine number and hydroxyl content delineated by the Tarrytown laboratory were reexamined. Samples of EPO high in iodine number, high in hydroxyl number and a blend of the two were compared to high quality EPO for compatibility. The results confirm and support the previous conclusions that i) excessive unsaturation contributes to plasticizer exudation (Iodine number ≥ 3.0), ii) excessive hydroxyl content aids exudation and iii) a blend of materials in (i) and (ii) will be worse in compatibility than either component.

b) Compatibility studies are in progress comparing UCC FLEXOL EPO with Argus Taft produced epoxidized soybean oil. The Argus "Drapex 6.8" may be resold as FLEXOL EPO.

(E.B. Harris)

DRY BLEND EXTRUSION RESIN (347 B 20)

1. DRY BLEND TEAM

BAKELITE resin QSAN-7 failed to qualify for a plant trial at Hatfield Wire and Cable Division because it was found to dry too rapidly as measured by the Hatfield laboratory test, at 100° C. Approval for a plant trial is dependent upon the resolution of dry blend characteristics as measured by UCC and Hatfield. At this point, it appears that the Hatfield test method is invalid because the Hatfield laboratory

had difficulty demonstrating that resins which had been used in their plant would fall within the specification limits (4.5 minutes, minimum to 6.5 minutes, maximum).

(L. G. Krauskopf)

2. DRY BLEND TESTING BY PROGRAMMED TEMPERATURE RISE

The laboratory method for measuring dry blending characteristics under high shear (thermally programmed No. 6 roller head) is beginning to generate meaningful data on various dry blend grade resins. Some variations in procedure continue to be investigated, but at this point it appears that optimum test conditions have been reasonably well defined.

(A. W. Conkling)

3. HENSCHEL SCALE-UP

a) Data has been collected on the dry blend cycle characteristics of a 5 lb., 50 lb., 100 lb., and 400 lb. Henschel mixer. The data are being considered and interpreted so that a report can be prepared on this phase of activity.

b) As an outcome of the Henschel scale-up trial at Prodex Corp., Fords, New Jersey, dry blend samples were extrusion coated on wire for testing. The only two materials from the trial that could be successfully extruded were the dry blends of BAKELITE resin QSAN-7, Blend 111 and Dow QX-3596. A dry blend of QSAN-7 blend 1750 from a 5 lb. Henschel run was also included in the extrusion coating for wire testing. The testing is in progress.

(T. A. Grillo)

PLASTICIZERS DERIVED FROM CAPROLACTONE (451 N 11)

1. CAPROLACTONE MONOMER

The project on determining the structure of a product produced by mixing vinyl resins and caprolactone monomer on a two roll mill has been terminated. An inadvertent mix-up of samples resulted in the analytical department receiving a vinyl film containing a known product. There does not appear to be any merit in pursuing the caprolactone monomer as a plasticizer. The correct samples do not exhibit a desirable degree of plasticization and have spewed after two months in storage at room conditions.

(E. B. Harris)

2. CROSSLINKED POLYBLENDS OF POLYCAPROLACTONE AND
POLY (VINYL CHLORIDE)

The change in physical properties of vinyl-poly caprolactone systems as a function of time and degree of crosslinking are being studied. After one month aging none of the crosslinked formulations changed whereas the unirradiated control did. A loss in low temperature impact resistance was measured. The ability to post process crosslinked samples decreased as the amount of crosslinking increased. One sample, highly irradiated, could not be processed as a thermoplastic.

(E. B. Harris)

3. 6-HEXANOYLOXYHEXYL-2-ETHYLHEXANOATE AND
METHYL-6-(6-ACETOXYHEXANOYLOXY) HEXANOATE

The evaluation of these materials as plasticizers for vinyl has been concluded with an assessment of staining characteristics when used in plastisol overlay flooring. Neither molecule performed adequately in stain resistance against an organic yellow dye. In addition, they did not possess the right combination of other performance properties to permit their use in vinyls at this time. Unless there are unique advantages to the use of plasticizers of this type, which may appear at a later date, this area of investigation will be inactive.

(E. B. Harris)

4. CAPROLACTONE - METHYL CAPROLACTONE COPOLYMERS

A 70/30 copolymer prepared by F. P. DelGiudice was received for comments on handling and processing as a vinyl plasticizer. In its present form, a rubbery, cold-flowing slab, it could be processed by compounding the vinyl formulation at the Banbury or mill. The operation would be slow, however, because of difficulty in cutting precise weights for the Banbury charge. If made available in pellet or crumb form, in mixture with vinyl resin, it could be handled as are nitrile rubber/vinyl polyblends. Manufacture of a form of the material that could be handled in conventional vinyl mixing systems would require process development work. Two alternatives are: a) co-precipitation from solution and b) latex co-coagulation of vinyl and caprolactone-methyl caprolactone polymers. Except for a property screening by D. H. Mullins at South Charleston, no additional work will be done on these systems.

(E. B. Harris)

PLASTICIZER SYNTHESIS (ALLOCATED)

1. NORBORNANE TRIESTERS

Examination of the spectrum of the volatile products from the reaction of di-2-ethylhexyl exo-5-norbornene-2,3-dicarboxylate and acetic acid, in the infrared, showed the presence of only a weak carbonyl band. The corresponding product from the endo compound gave a strong $C=O$ stretching absorption and led to the assignment of 2-ethylhexyl acetate as its structure.

Gas chromatograms of the liquids from both the endo and the exo compounds exhibited two peaks with identical retention times. They differed, however, in that, in the case of the exo compound the more volatile component was present in excess (95%), while in the case of the endo, the less volatile component predominated (93%). The liquid from the exo compound was further distilled on a spinning band column in order to obtain a pure sample so that additional characterization may be carried out. Since the formation of these byproducts serve as indicators for the internal transesterification reaction of the assumed triester intermediates, any conclusions as to the success of the addition reaction must be postponed until characterization of these compounds is accomplished.

2. ALDEHYDE - EPOXIDE REACTION

The product from the reaction of n-heptaldehyde with stilbene oxide gave a positive hydroxamic acid test, further supporting the assignment of an ester structure to it. The product is presently undergoing lithium methoxide transesterification for determination of the alkyl portion.

Additional stilbene oxide was prepared for further studies on this reaction and in that referred to below.

3. BUTYL BENZYL PHTHALATE DIMER

The reaction of the monobutyl ester of phthalic acid with stilbene oxide in the presence of an organic base (triethyl amine) has proved unsuccessful. Other reaction conditions will be attempted.

(S. Solomon)

W. H. Bauer/rm

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(S. Solomon)

W. H. Bauer/rm

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