STATUS REPORT

EXPLORATORY VINYL RESIN SCREENING
PRELIMINARY EVALUATION OF EXPERIMENTAL VINYL CHLORIDE-VINYL ACETATE-ETHYLENE TERPOLYMERS

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SUMMARY The preliminary comparative evaluation in a simple rigid formula of four experimental vinyl chloride-vinyl acetate-ethylene terpolymers prepared at Texas City in pilot-scale facilities with a sample of VYFS resin indicates the following: (a) The inclusion of ethylene in a vinyl chloride-vinyl acetate copolymer of approximately 85:15 ratio results in a reduction in melt viscosity, lower tensile strength (with accompanying increased elongation) and significant lowering of the heat distortion temperature. (b) Brittleness temperature is essentially unchanged.

The relatively significant reduction in heat distortion temperature suggests that ethylene content of these terpolymers will have to be limited for use in rigid applications.

Evaluation of additional samples of VYCA, VYCR and experimental terpolymers and further study will be required to define the quantitative relative effects of inherent viscosity differences and variation in composition on the property changes observed.

DISCUSSION

Polymer Description

The composition of the polymers studied is documented in the following table:

Resin	Vinyl Chloride, %	Vinyl Acetate, %	Ethylene, %	η inh
QEX-1174	85.8	12.8*	1.4	0.539
QEX-1175	86.5	12.6*	0.85	0.550
QEX-1221	85.3	13.7*	1.0	0.530
QEX-1222	85.5	14.0*	0.5	0.528
VYFS Blend 3125	85.5	14.5	0	0.510

*By difference.

Research and Development Department
Chemicals Division
Union Carbide Corporation

The samples were prepared using the Process-10 recipe. Vinyl chloride content was defined using the Paar bomb technique. Ethylene content was defined using infrared techniques, and the absorption curve reference utilized with vinyl chloride-ethylene copolymers. (Whether this represents a good estimate of actual ethylene content has yet to be established.) For the purpose of this report, the analyses are assumed to accurately represent the polymer composition.

The samples evaluated differ both in inherent viscosity and composition (Table I). Because of these differences, only generalized statements relating to the influence of these variables on changes in processing and physical properties can be made from the limited number of samples evaluated.

The major purpose of this report is to document the properties which will form a base point for comparison as additional evaluations are conducted.

Physical Properties

The preliminary evaluation of physical properties was limited to a single rigid formulation containing 100 parts resin, 2 phr Dyphos (dibasic lead phosphite), and 1 phr DS207 (dibasic lead stearate).

Tensile Strength and Elongation

The accumulated tensile data (Table II) suggest that the inclusion of ethylene results in a reduction in tensile strength and increase in tensile elongation. This phenomenon is observed when the properties of the QEX-1221 and QEX-1222 samples are compared and when the tensile strength of the VYFS sample is compared to that of the experimental resins.

The relatively high tensile strength of QEX-1222 sample may be due to the combination of low ethylene content (0.5 per cent) as well as a relatively high inherent viscosity compared to the VYFS sample (0.53 to 0.51).

Brittleness Temperature

The data shown in Table II suggests that neither molecular weight differences nor the inclusion of ethylene significantly changes the brittleness temperature of the resins studied, though the resin with the highest ethylene content (1.4 per cent) does show a 3°C lower reading than the VYFS resin.

Heat Distortion Temperature

The heat distortion temperature decreases proportionately with increasing amounts of ethylene in the polymer. The data plotted in Figure 1 illustrates the change. This chart suggests that the amount of ethylene included in the terpolymer will have to be limited

in resins intended for rigid applications where there is a critical heat distortion temperature requirement.

Thermal Stability

The relative thermal stability was assessed using the Copolymer Resin Mill Test (CRMT). The data shown in Table III reveals that the stability of the QEX-1221 and QEX-1222 samples is superior to that of the QEX-1174 and QEX-1175 samples; the stability of the former two resins is judged at least equivalent to that of the VYFS control sample. No reason for the apparent differences in th rmal stability of the experimental resins may be advanced at this time.

Conclusions of Physical Property Study

The following tentative observations may be drawn from the data:

a. Tensile strength is lowered by the inclusion of ethylene.

b. Tensile elongation is lowered by both reduction in molecular weight and a decrease in the amount of ethylen in the terpolymers.

c. Brittleness temperature is not significantly influenc d by the inclusion of ethylene in the range of compositions studied.

d. Heat distortion is the physical property most influenced by the inclusion of ethylene. The heat distortion temp rature decreases proportionately with increasing amounts of ethylene.

Processibility

The relative processibility of the resins was studied using the C. W. Brabender Plasti-Corder. Two test conditions were used: (A) using a head temperature of 168°C and (B) using a head temperature of 140°C (both at 40 rpm). The formulation is the same as that used to obtain physical properties. The data listed in Table IV permits the following tentative observations:

1. The inclusion of ethylene results in a reduction in the apparent melt viscosity (readily observed in data obtained using Condition "A") as well as in the lower melt viscosity of QEX-1222 vs QEX-1221 as defined for both conditions.

2. The use of the lower head temperatures in the plastograph yields higher melt viscosity and larger over-all differences between samples. The use of the lower head temperature, however, yields data characterized by significantly different temperatures (152-160°C) at equilibrium melt viscosity which makes interpretation more difficult.

All of the resins (including the VYFS resin) showed immediate fluxing in the plastograph even when the lower head temperature was employed. Additional study of the relative fluxing t mperature of these resins is planned following a procedure suggested by Mr. P. T. McCoy of the Tarrytown Laboratory*:

Future Studies Planned

The evaluation of additional samples, of VYCA and VYCR, resins of selected inherent viscosity as well as of other vinyl chloride-vinyl acetate-ethylene terpolymers including the QEX-1226 sample is planned. The latter resin (85.5 per cent vinyl chlorid , 1.0 per cent ethylene, η inh = 0.575) and QEX-1221 resin discuss d in this report have been sampled for evaluation to selected flooring customers based on an earlier evaluation of QEX-1174 and -1175 in a vinyl asbestos formulation by Mr. McCoy of the Tarrytown Laboratory. The study showed that the terpolymers were more efficient (required lower plasticizer content to yield comparable tile properties) than copolymers of comparable vinyl chloride content and inherent viscosity (1).

PERIOD COVERED:
LABORATORY ACCOUNT:

Attachments:
4 Tables
1 Figure

J. W. Fields

* Unpublished Report, P. T. McCoy

(1) McCoy, P. T. and Conkling, A. W., Performance of Vinyl Chloride-Vinyl Acetate-Ethylene Terpolymers in a Typical Vinyl Asbestos Formulation, Memorandum to Mr. E. R. Weidlein, Jr., Research and Development Department, Tarrytown, New York, October 6, 1965.

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TABLE I

GENERAL PROPERTIES OF EXPERIMENTAL
VINYL CHLORIDE-VINYL ACETATE-ETHYLENE TERPOLYMERS

Resin Designation	QEX-1174	QEX-1175	QEX-1221	QEX-1222	VYFS Blend 3125
Poly(vinyl chloride) % (WC-294-A)	85.8	86.5	85.3	85.5	85.5
Ethylene Content,%*	1.4	0.85	1.0	0.5	0
Inherent Viscosity (ASTM D-1243 Method A)	0.539	0.550	0.530	0.528	0.510
Apparent Density, lb/ft^3	36.9	36.4	37.8	40.2	33.3
ASTM Flow Time, sec/400 cc	3.2	3.3	3.4	4.0	5.2
ASTM Plasticizer Sorption, %	65	55	58	51	74
Sieve Analysis, P r Cent Through Mesh 40	100	99.8	100	99.8	99.8
60	99.8	82	99.5	97.8	98
80	94	65	95	92	93
100	87	56	85	84	86
120	78	50	72	76	79
140	54	41	43	59	67
200	25	25	14	35	47
270	10	12	5	18	29
325	4	7	2	10	17
Median Particle Size, Microns	103	132	111	93	78

*Infrared Analysis

TABLE II

PHYSICAL PROPERTIES

Resin Designation	QEX-1174	QEX-1175	QEX-1221	QEX-1222	VYFS Blend 3125
Brittleness Temperature (WC-76-A-2)	+41°C	+44°C	+43°C	+46°C	+44°C
Heat Distortion Temperature (ASTM-648-56)	53°C	55°C	55°C	57°C	63°C
Tensile Strength, psi (23-261-19)	4670	4770	4780	5120	4900
Tensile Elongation, per cent (23-261-19)	68	67	96	92	38
Yield Strength, psi (23-261-19)	7230	7100	6570	7180	7220
Yield Elongation, per cent (23-261-19)	3.0	3.0	2.9	3.0	3.0

Formulation

Resin	100 phr
Dyphos (dibasic lead phosphite)	2 phr
DS 207 (dibasic lead stearate)	1 phr

Processing Conditions

Roll Mill Surface Temperature	155°C
Milling Time	5 minutes
Press Platen Temperature	160°C
Press Time	5 minutes

TABLE III

RELATIVE THERMAL STABILITY
(Copolymer Resin Mill Test)

Reflectance at 400 mμ
Beckman Model B Modified Spectrophotometer

	Reflectance Readings				
Resin	QEX-1174	QEX-1175	QEX-1221	QEX-1222	VYFS Blend 3125
Milling time, 5 minutes	20	23	38	40	34
10 minutes	7	7	13	15	16
15 minutes	5	5	9	9	6
20 minutes	4	5	8	8	5
CRMT*	27	30	51	65	50
Holding Power, %**	45	43	45	45	45

*CRMT = The addition of the 5-minute and 10-minute reflectance r adings.

**Holding Power is calculated by the following formula:

$$\frac{\text{5-Minute Reading X 4}}{\text{5 + 10 + 15 + 20-Minute Readings}}$$

TABLE IV

APPARENT EQUILIBRIUM MELT VISCOSITY

(15 Minutes after Peak Torque-
C. W. Brabender Plasticorder)*

(A) Jacket Temperature 168°C; Rotor Speed 40 rpm Sample Size = 59 grams

Resin	Apparent Melt Viscosity, Meter-Grams-Sec^{-1}	Compound Temperature
QEX-1174	1000	167°C
QEX-1175	950	168°C
QEX-1221	1000	168°C
QEX-1222	1100	169°C
VYFS, Blend 3125	1100	167°C

(B) Jacket Temperature 140°C; Rotor Speed 40 rpm

QEX-1174	1780	154°C
QEX-1175	1860	152°C
QEX-1221	1660	155°C
QEX-1222	1730	155°C
VYFS, Blend 3125	1860	160°C

Formulation

Resin	100 phr
Dyphos**	2 phr
DS-207***	1 phr

*Under the conditions studied, all compounds yielded immediat fluxing.

**Dyphos is dibasic lead phosphite, a powdered stabilizer available from the National Lead Company.

***DS-207 is dibasic lead stearate.

HEAT DISTORTION TEMPERATURE VS ETHYLENE CONTENT

OF VINYL CHLORIDE-VINYL ACETATE-ETHYLENE TERPOLYMERS

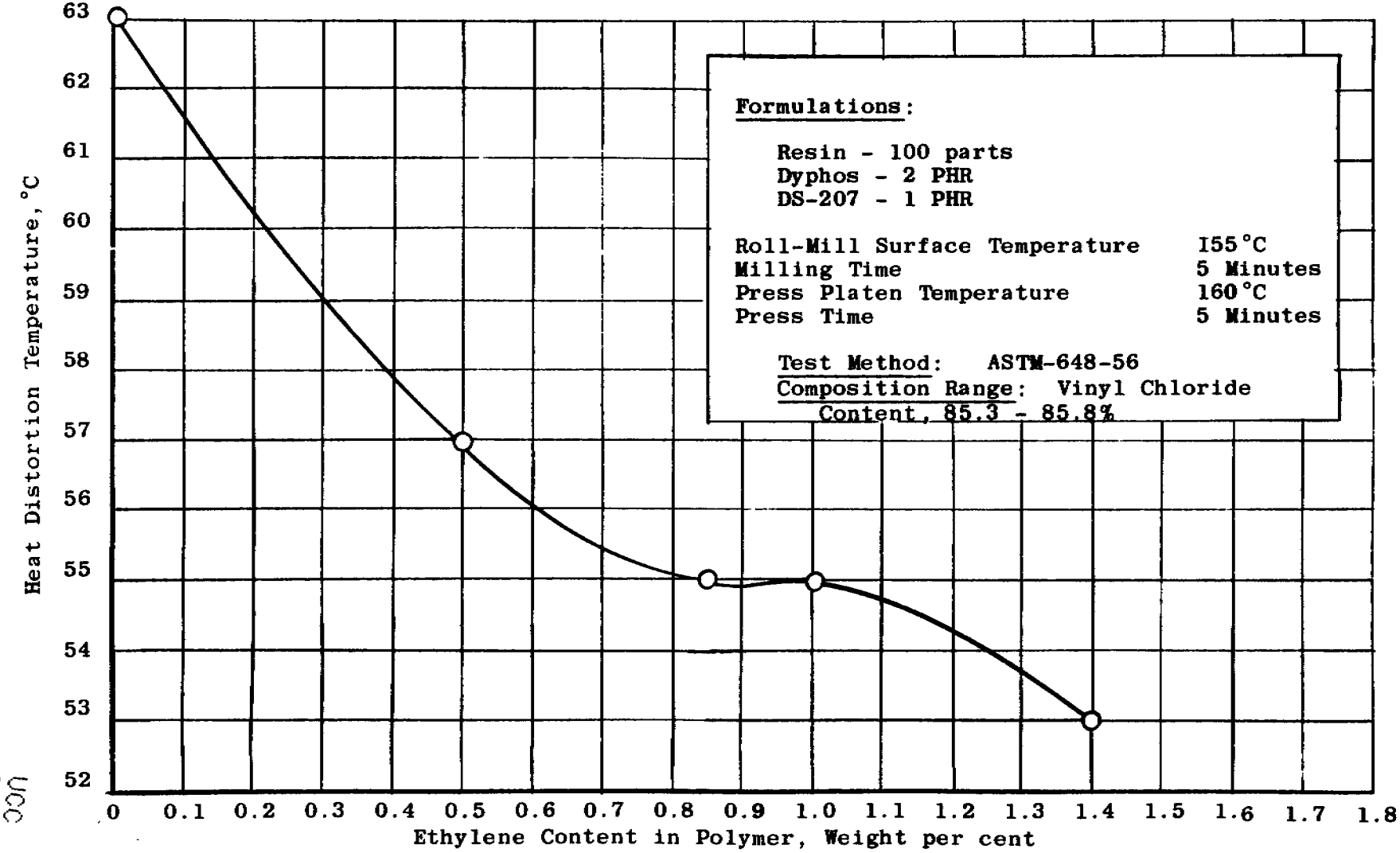

FIGURE 1

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