BUSINESS CONFIDENTIAL

PROJECT REPORT

THIXOTROPIC POLYESTERS

EFFECT OF UCC ASBESTOS R-G244 IN POLYESTERS

AUTHORS: L. R. Comstock

SUPERVISOR: P. L. Smith

DATE: September 6, 1967

PROJECT NO.: 342A25

FILE NO.: 8245

SUMMARY Union Carbide's Resin Grade Asbestos (R-G244) provides a thixotropic polyester with a viscosity about four times that attainable with an equal amount of CAB-O-SIL. The addition of a small amount (0.5-2.0 weight per cent) of a hydroxyl-containing compound, such as glycerol, to the polyester, however, increases the effectiveness of CAB-O-SIL to equal that of R-G244. Even so, R-G244 provides the advantages of lower cost and leads to thixotropic polyesters with excellent clarity.

The effect of R-G244 and CAB-O-SIL on polyester activity is identical. At a 2.0 per cent level, activity is decreased only slightly.

The R-G244 containing polyester has a slower rate of viscosity recovery after shear than does the polyester thickened with CAB-O-SIL. Whether this is an advantage or disadvantage will depend on the degree of sagging when sprayed onto a vertical surface and on rate of penetration into the glass fibers to which the polyesters are applied. Due to the limitations of our test designed to determine viscosity recovery, measurements under conditions which more nearly simulate fabricating conditions are being made at Niagara Falls. In addition to this test, the effect of R-G244 on storage stability of polyesters also is being determined.

Assuming that the results of these further tests indicate no major disadvantages, R-G244 appears to be superior to CAB-O-SIL on a cost-performance basis. In polyesters, there is a potential annual market for about 0.5-1.0 MM pounds of R-G244.

INTRODUCTION An asbestos product (R-G244), which has different surface properties than those of the chrysotile fiber from which it is derived, was developed by UCC at Niagara Falls. This product is prepared by adding sodium silicate to an aqueous slurry of asbestos fiber followed by near neutralization with acetic acid.[1] Byrne and Chwastiak recently reported R-G244 to be more effective than the currently used CAB-O-SIL for thickening polyesters. R-G244 is being offered for 60 cents/pound while CAB-O-SIL sells for 75 cents/pound.

RESEARCH AND DEVELOPMENT DEPARTMENT
CHEMICALS AND PLASTICS
UNION CARBIDE CORPORATION
South Charleston, West Virginia

The objective of this study was to investigate further the merits of R-G244, as a thixotropic filler relative to CAB-O-SIL M-5 in a general purpose polyester.

DISCUSSION

I. Viscosity of Polyester Disperions at Equilibrium.

Dispersions of R-G244 and CAB-O-SIL M-5 were prepared by mixing with a general purpose polyester (Rohm and Haas P-43 diluted to 40 per cent styrene) for 15 minutes in a laboratory scale Cowles Dissolver.. After standing in a constant temperature bath (25°C.) for 24 hours, viscosity was measured with a Brookfield Viscometer, Model LVT, using a number 4 spindle at 6 and 60 rpm.

Visual observations of the dispersions revealed that mixtures containing as much as 2.0 per cent R-G244 were clear while as little as 0.5 per cent CAB-O-SIL gave milky dispersions. Table I and Figure 1 show that R-G244 is a much more effective thickener for the polyester resin system. At a 2.0 per cent level, R-G244 provided a viscosity more than four times that of the CAB-O-SIL. These data compare quite well with the results reported by Byrne and Chwastiak(1) in their initial evaluation of R-G244 in this polyester. We noted, however, that some settling of both fillers occurred when concentrations of less than 1.0 per cent were used.

II. Viscosity Recovery of Thixotropic Polyesters after Shear.

When thixotropic polyesters are sprayed onto vertical surfaces there is a considerable viscosity drop as it passes through the spray orifice. To prevent sagging or run-off and loss of polyester, which increases cost and leads to a product non-uniform in composition or thickness, rapid viscosity recovery is necessary.

To determine the relative rate of viscosity recovery of a general purpose polyester containing R-G244 and CAB-O-SIL, dispersions of 1.5 per cent R-G244 and 2.5 per cent CAB-O-SIL, which were prepared in the Cowles Dissolver and allowed to reach an equilibrium viscosity at room temperature, were stirred with a high speed mixer for 15 minutes and immediately placed in a Brookfield Viscometer. Their viscosities were measured at 1.0 minute intervals. This study (Table II and Figure 2) showed that the viscosity of the CAB-O-SIL dispersion approached complete viscosity recovery (97 per cent) in 3.0 minutes while the R-G244 dispersion required about 5.0 minutes.

This test procedure had several limitations such as bubbles introduced into the dispersion during stirring and time lapse during the transfer of the samples from the high speed stirrer to the viscometer. Based on these limitations the results of this study may not be completely accurate. A better test would involve the actual spraying of the thixotropic polyester, at pressures normally used during spray-up application, into a vessel suitable for an immediate viscosity determination or onto a vertical surface and compare the degree of sagging. This test is being studied by Mr. R. E. Byrne at Niagara Falls.

III. Effect of Hydroxyl on Viscosity.

When colloidal silicas are used as the thixotropic fillers in polyesters for hand lay-up or spray-up application, a small amount of a polyol, such as glycerol, is normally used to increase the effectiveness of the silica.(2) For example, the addition of 2.0 per cent glycerol to the general purpose polyester containing 2.0 per cent CAB-O-SIL increases viscosity from 7,000 to 40,000 cps. Glycerol can be added during the preparation of the dispersion or can be added later to the dispersion. In either case the polyester dispersion is allowed to stand at room temperature to reach an equilibrium viscosity.

Table III shows that the added glycerol has a much greater influence on the thixotropic effectiveness of CAB-O-SIL than it does on R-G244. The addition of as little as 0.5 per cent glycerol to a general purpose polyester containing the same concentration of CAB-O-SIL and R-G244 leads to dispersions with similar viscosities.

These data suggest that the relative effectiveness of R-G244 and CAB-O-SIL will vary depending on the hydroxyl content of the polyester. When added to a polyester with a high hydroxyl number or water content, CAB-O-SIL may approach the thixotropic effectiveness of the R-G244.

IV. Activity of Thixotropic Polyesters.

The effect of R-G244 and CAB-O-SIL, at a 2.0 per cent level, on the polyester activity was measured, using the standard SPI Gel Test at 80°C. The following results show that both of the thixotropic fillers have about the same affect and reduce activity only slightly.

	SPI Gel Test		
	Gel Time Min./Sec.	Exotherm Temp., °C	Exotherm Time Min./Sec.
P-43	3/28	231.5	6/27
P-43 + 2.0% R-G244	4/9	233	6/52
P-43 + 2.0% CAB-O-SIL	4/4	234	6/17

CONCLUSIONS AND RECOMMENDATIONS In comparison to CAB-O-SIL, Carbide' new silica treated asbestos, R-G244, is more effective for the preparation of thixogropic polyesters. R-G244 also has the advantage of lower cost and does not impart haze to the polyester. When a small concentration of glycerol is added to the polyester, however, the effectiveness of CAB-O-SIL increases to a much greater extent than does R-G244.

After dispersions containing R-G244 and CAB-O-SIL have been subjected to shear the one containing R-G244 recovers its initial viscosity at a slower rate. This may be a disadvantage of R-G244 since spray-up application to a vertical surface results in a viscosity drop and if the recovery rate is too slow sagging of the polyester may occur. The slower viscosity recovery of the R-G244 system may, however, be an advantage if the rate of recovery is fast enough to prevent sagging but slow enough to allow better penetration of the polyester into the glass fibers on which it is applied. Due to the limitations of our test procedure it will be necessary to further check the effect of viscosity rate on performance under conditions which simulate those of actual practice before it can be considered a limitation or advantage of R-G244.

Although we plan no further work on the evaluation of R-G244 in polyesters, experiments are in progress at Niagara Falls to check our findings on viscosity recovery rate and to determine the effect of R-G244 on polyester storage stability.

The data contained in this report will be used to prepare a Technical Information brochure.

BIBLIOGRAPHY

(1) Byrne, R. E. and Chwastiak, S.; The Chemical Modifications of UCC Chrysotile Asbestos, Silica Modification for Viscosity Control; July 11, 1967.

(2) Cabot Corporation, Technical Information Sheet CPLA-3.

ATTACHMENTS 3 Tables
2 Figures

eh

Lowell R. Comstock

TABLE I

EFFECT OF R-G244 AND CAB-O-SIL ON VISCOSITY OF A GENERAL PURPOSE POLYESTER(1)

	Brookfield Viscosity, cps at 25°C(2)	
R-G244, %	6 rpm	60 rpm
0	500	400
0.5	1000	600
1.0	3900	870
1.5	8900	2240
2.0	31000	6200
CAB-O-SIL, %		
0	500	400
0.5	600	500
1.0	1000	600
1.5	2400	660
2.0	7100	1450

(1) Rohm and Haas P-43 with 40% styrene.

(2) Model LVT, No. 4 spindle.

BUSINESS CONFIDENTIAL
342A25

TABLE II

VISCOSITY RECOVERY OF THIXOTROPIC POLYESTERS[1] AFTER SHEAR[2]

	Viscosity, cps @ 25°C.[3]		
Asbestos R-G244	Time, min. after shear	6 rpm	Percent Recovery
1.5%[4]	1.0	5500	52
	2.0	8500	81
	3.0	9200	88
	4.0	9700	92
	5.0	10000	95
	6.0	10250	98
	7.0	10250	98
CAB-O-SIL M-5			
2.5%[5]	1.0	11000	80
	2.0	12900	94
	3.0	13200	97
	4.0	13300	97
	5.0	13300	98
	6.0	13400	98
	7.0	13400	

(1) Rohm and Haas P-43 (40% styrene).
(2) Mixed 15 minutes with a high speed mixer.
(3) Brookfield Viscosity, Model LVT, #4 spindle.
(4) Viscosity before shear = 10500 cps.
(5) Viscosity before shear = 13700 cps.

TABLE III

EFFECT OF HYDROXYL ON THE VISCOSITY OF THIXOTROPIC POLYESTERS(1) BROOKFIELD VISCOSITY, CPS @ 25°C(2)

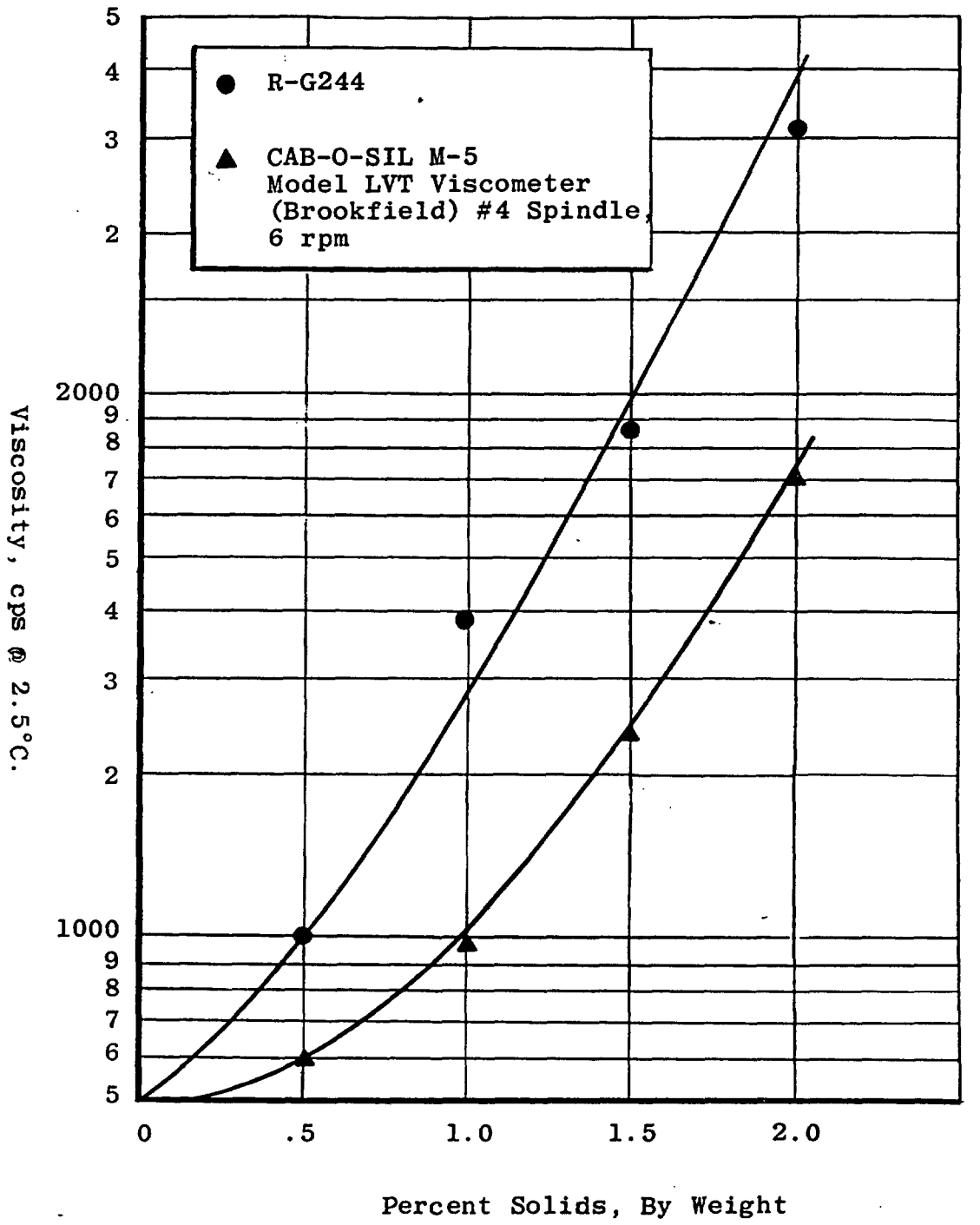
Asbestos R-G244	Glycerol	Brookfield Viscosity, cps @ 25°C.(2) 6 rpm	60 rpm
1.0%	0%	3900	870
1.0%	0.5%	7300	1980
1.0%	2.0%	9300	2850
2.0%	0%	31000	6200
2.0%	2.0%	36400	9680
CAB-O-SIL M-5	**Glycerol**		
1.0%	0%	1000	600
1.0%	0.5%	7300	2200
1.0%	2.0%	11700	2950
2.0%	0%	7100	1450
2.0%	2.0%	40500	7650

(1) Rohm and Haas P-43 (40% styrene).

(2) Model LVT #4 spindle.

BUSINESS CONFIDENTIAL
342A25

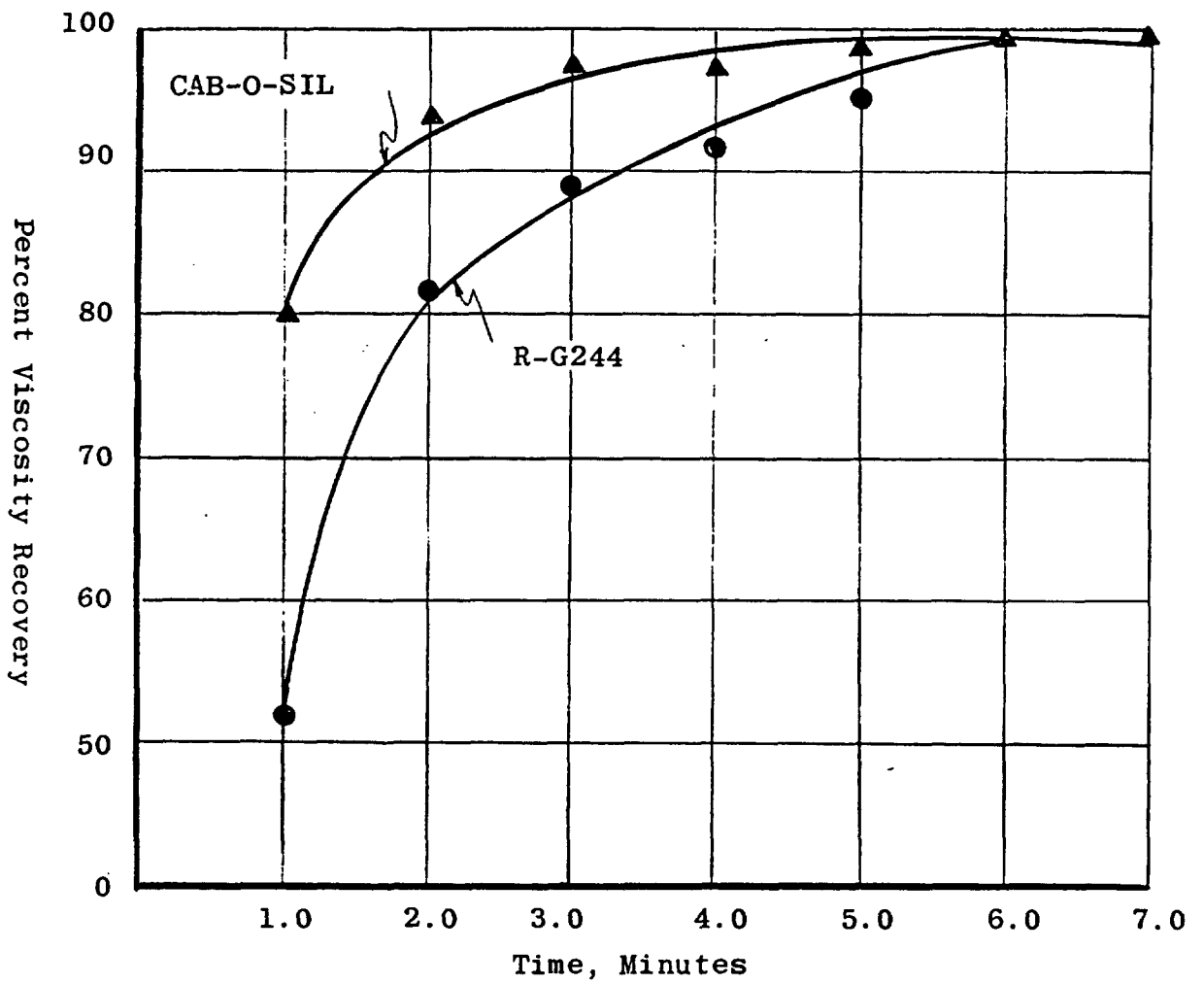
FIGURE 1



BUSINESS CONFIDENTIAL
342A25

FIGURE 2

Viscosity Recovery of Thixotropic Polyesters After Shear



BUSINESS CONFIDENTIAL
342A25

DISTRIBUTION

Mr. R. H. Bruce, NYO-46
Mr. R. E. Byrne, Jr., Niagara Falls
Mr. W. L. Dykes, 511
Mr. D. D. Lee, NYO-32
Dr. C. W. McGary, 511
Mr. H. B. Reese, NYO-16
Mr. N. J. Setter, NYO
Mr. J. J. Smith, 511
Mr. P. A. Thomas, 312
Mr. H. P. Vinyard, 511
Mr. R. G. Woolery, Niagara Falls
Authors
Information Retireval