UC-1541

DLE
you may be interested in this - file - Library - 770
JWB

G

THE CHEMICAL MODIFICATION OF UCC CHRYSOTILE ASBESTOS
I. SILICA MODIFICATION FOR VISCOSITY CONTROL

by

R. E. Byrne, Jr.
S. Chwastiak

July 11, 1967

RECEIVED
JUL. 17 1967
J. W. BIDDLE

Research and Development Department
Union Carbide Corporation
Chemicals & Plastics Operations Division
Niagara Falls, N.Y.

I-198

BUSINESS CONFIDENTIAL

tabbies
PLAINTIFF'S EXHIBIT
UC-1541

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/1

THE CHEMICAL MODIFICATION OF UCC CHRYSOTILE ASBESTOS I. SILICA MODIFICATION FOR VISCOSITY CONTROL

by

R. E. Byrne, Jr.
S. Chwastiak

July 11, 1967

Group Manager - R. G. Woolery

Project No. 885-28-2-52

Research and Development Department
Union Carbide Corporation
Chemicals & Plastics Operations Division
Niagara Falls, N.Y.

BUSINESS CONFIDENTIAL

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/2

TABLE OF CONTENTS

	Page No.
Introduction	1
Summary	1
Discussion	2
General	2
Testing Procedure	2
Conditions of Preparation	6
Competitive Asbestos	14
Pilot Plant Production of Treated Asbestos	15
Properties of Silica-Treated Asbestos	18
Mechanism of Silica Treatment	22
Mechanism of Thickening Polyester by Asbestos Products	25
Product Utilization	26
Patent Position	28
Conclusions	29
Appendices	30
References	43

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/3

LIST OF APPENDICES

Appendix No.		Page No.
1	- Silica Treatment of Asbestos at Various pH Values	30
2	- Analyses of Products from Silica Treatment at Various pH Values	31
3	- Silica Treatment of Asbestos at pH 8 with Different Amounts of Sodium Silicate	32
4	- Analyses of Products from Silica Treatment of Asbestos Made with Different Additions of Sodium Silicate	33
5	- Silica Treatment of Acidified Asbestos Suspensions with Different Amounts of Sodium Silicate	34
6	- Analyses of Products from Silica Treatment of Acidified Asbestos Suspensions Made with Different Additions of Sodium Silicate	35
7	- Silica Treatment of HPO Asbestos Opened Further in a Waring Blendor	36
8	- Thickening of Polyester by Silica-Treated HPO Asbestos Opened Further in a Waring Blendor	37
9	- Analyses of Products from Silica Treating HPO Asbestos Opened Further in a Waring Blendor	38
10	- Effect of Temperature on Silica Treatment of Asbestos	39
11	- Analyses of Products from Silica Treatment of Asbestos at Different Temperatures	40
12	- Thickening of Polyester by Pilot Plant Product from Run 59A	41
13	- Thickening of Polyester by Cab-O-Sil	42

LIST OF FIGURES

Figure No.		Page No.
1	- Effect of Asbestos and of a Colloidal Silica on the Viscosity of a Polyester Resin	3
2	- Viscosity of Polyester Resin Containing Various Additions of Particulate Solids	5
3(a)	- Thickening of Polyester Resin by Asbestos Treated with Silica at Various pH Values	7
3(b)	- Recovery of Silica on Asbestos by Treatment at Various pH Values	7
4(a)	- Thickening of Polyester Resin by Asbestos Treated at pH 8 with Different Amounts of Silica	9
4(b)	- Recovery of Silica on Asbestos During Treatment at pH 8 with Different Amounts of Silica	9
5(a)	- Thickening of Polyester Resin by Asbestos Treated with Different Amounts of Silica in Acidified Suspensions	10
5(b)	- Recovery of Silica on Asbestos by Treatment in Acidified Suspensions	10
6	- Replica of Asbestos Flake	11
7(a)	- Retention on 10-Micron Sieve of Asbestos Opened in a Waring Blendor	13
7(b)	- Effect of Liberation on Thickening of Polyester Resin by Silica-Treated Asbestos	13
8	- Comparison of Thickening of Polyester Resin by Treated Asbestos from Pilot Plan Run 59A with Colloidal Silica and with Untreated Asbestos	17
9	- Zeta Potentials of Treated Asbestos Slurry and of Treated Asbestos After Drying	21
10	- Adsorption of Methylene Blue on Asbestos Products	23
11	- Effect of Shear Rate on Measured Value of Apparent Viscosity of Polyester Suspensions	27

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/5

LIST OF TABLES

Table No.			Page No.
I	-	Effect of Neutralization on Recovery of Silica	4
II	-	Effect of Temperature on Silica Treatment of Asbestos	14
III	-	Silicate Treatment of Competitive Asbestos Materials	15
IV	-	Effect of Asbestos Liberation During Silica Treatment in the Pilot Plant	15
V	-	Effect of pH on Silica Treatment of Asbestos in the Pilot Plant	16
VI	-	Physical Properties of Asbestos, Treated Asbestos, and Cab-O-Sil	18
VII	-	Typical Analyses of Silica-Treated Asbestos	18
VIII	-	Properties of Silica-Treated Asbestos	20
IX	-	Polyester Thickening by Asbestos Treated with Aged Silica Solutions (Polymerized)	24
X	-	Effect of Mixing Time on Treated Asbestos in Polyester Resin	26

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/6

Niagara Falls, New York
July 11, 1967

THE CHEMICAL MODIFICATION OF UCC CHRYSOTILE ASBESTOS
I. SILICA MODIFICATION FOR VISCOSITY CONTROL

INTRODUCTION

Late in 1965, market research and field evaluations indicated that a low-moisture content version of our regular High Purity Asbestos had some merit as a general purpose thickener in resin systems. Such a material, known as Resin-Grade Asbestos 144 (R-G144), was introduced to the market with subsequent sales of about 100 tons in 1966. It was used primarily in high-viscosity adhesives, sealants, caulks, and sound deadeners. Anticipated sales for this product are about 1000 tons in 1967 at a price of $.10/pound (f.o.b. King City, California).

Attempts to use R-G144 for thixotropy development in low-viscosity systems, such as polyester laminating resins and the like, however, exposed several product limitations. Resulting mixes exhibited poor color and a tendency toward rapid settling. A laboratory program was begun to overcome these problems. An outgrowth of this work has been the development of a new product, R-G244, which is the subject of this report.

SUMMARY

An asbestos product has been made which has radically different surface properties than those of the chrysotile fiber from which it was derived. It was developed specifically for viscosity control applications in polyester resins which are presently being thickened largely with high-priced colloidal silicas. Normal asbestos is less effective than colloidal silicas in thickening efficiency, but treated asbestos is superior to silica.

The preferred process consists of adding sodium silicate, at a rate of 8 to 10 pounds of silica per 100 lb. of asbestos, to an aqueous slurry of well liberated asbestos fibers, and then reducing the pH of the slurry to 8.0 with acetic acid. Alternatively, it is possible to add a calculated quantity of acid to the slurry and adjust the final pH to 8.0 with sodium silicate.

The critical step in the process is the preparation of an asbestos feed which is sufficiently well liberated. A slurry of asbestos which contains less than 4 per cent by weight of solids retained on a 10-micron sieve has been found to be acceptable feed material.

Several successful pilot plant runs have been made, showing that the conditions for treatment based on laboratory studies are adequate to produce satisfactory product.

The mechanisms of silica treatment and of polyester thickening are discussed. Some of the intrinsic properties of the treated asbestos are reported.

DISCUSSION

General

Many uses of polyester resins in coating or molding result in sagging of the resin on vertical surfaces. Additives, such as colloidal silica, are often used to thicken the resin system and overcome this tendency in automotive bodies, boats, etc. R-G144 asbestos was tried in this area as a potential replacement for silica. Figure 1 shows the relative thickening effects of silica and R-G144 in a typical polyester system.

Even if both silica and asbestos, when dispersed in a liquid system, could form a continuous structure, it was expected that asbestos would show the greater effect on viscosity because of its fibrous shape. That this was not the case could possibly be explained on the basis of a particle size which was too large or on the basis of the difference in surface properties between the two minerals. Chrysotile asbestos is one of the few naturally occurring minerals which is positively charged up to pH values of 11 or 12. Martinez & Zucker(1), however, have reported that this surface charge can be changed in sodium silicate solutions so that at concentrations greater than about 10^{-2} m./l., the charge becomes negative. It has been our experience that silica can be fixed on the asbestos surface by acidifying an asbestos-sodium silicate slurry. Table I presents data showing the charge reversal of asbestos and recovery of silica on the asbestos after reducing the pH of an asbestos slurry containing 12 parts of SiO_2 (added as sodium silicate) per 100 parts of asbestos.

Asbestos treated in this manner was found to be an effective thickener for polyester resins. Typical initial data are shown in Figure 2, where the chrysotile asbestos (R-G144), Cab-O-Sil, and treated asbestos (R-G244) are compared for this use. It became apparent immediately that the treatment produced a superior product, so an experimental program was started to define the best conditions for the treatment.

Testing Procedure

The procedure for each test consisted of the following basic steps:

1. Separation of the fibers into discrete fibrils in an aqueous slurry, usually 2.5 liters of a 1% suspension thrashed for 3 minutes in a large Waring Blendor

2. Addition of the reagents, sodium silicate and acetic acid, usually as 1 molar solutions

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chrysotil... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 8 of 49 asbestosclaims.law/library/16643/8

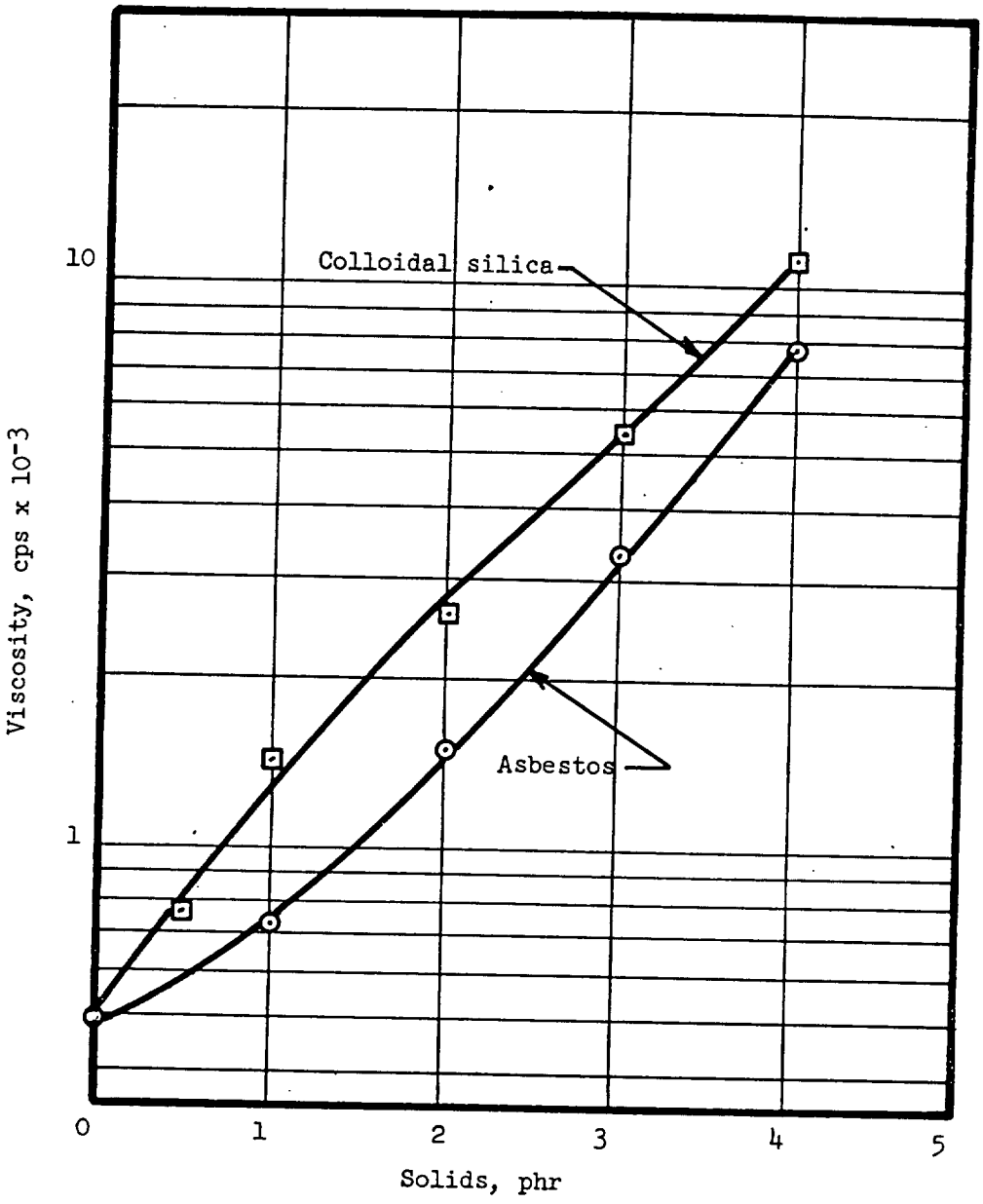


FIGURE 1 - EFFECT OF ASBESTOS AND OF A COLLOIDAL SILICA ON THE VISCOSITY OF A POLYESTER RESIN

Resin - Crystic 191E

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chrysotil... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 9 of 49 asbestosclaims.law/library/16643/9

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso...
ACL Doc 16643 · Page 10 of 49

TABLE I

Effect of Neutralization on Recovery of Silica

Test No.	Treatment	Sod. Silicate Added, SiO_2, pha(3)	Filtrate Analysis SiO_2, g./l.	Rec. of(1) SiO_2 on Asb., %	"Free" SiO_2(2) on Asb., pha (3)	Sign of(4) Surface Charge
1	Susp., 1% asb., pH = 9.2	0	<0.005	0	0	pos.
2	Sod. silicate added, pH = 12.1	12	0.99	17	2.1	pos.
3	Sod. silicate added, neutralized with acetic acid, pH = 9.6	12	0.50	58	7.0	neg.

(1) Recovery of SiO_2 on the asbestos is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

(2) "Free" SiO_2 is calculated as the difference between the total SiO_2 assay of the product and the amount of SiO_2 in the asbestos lattice itself, assuming an analysis of 41.5% MgO, 41.4% SiO_2 for the asbestos.

(3) pha - parts per hundred parts of asbestos

(4) Sample washed to neutral pH before measurement by electro-osmosis.

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/10

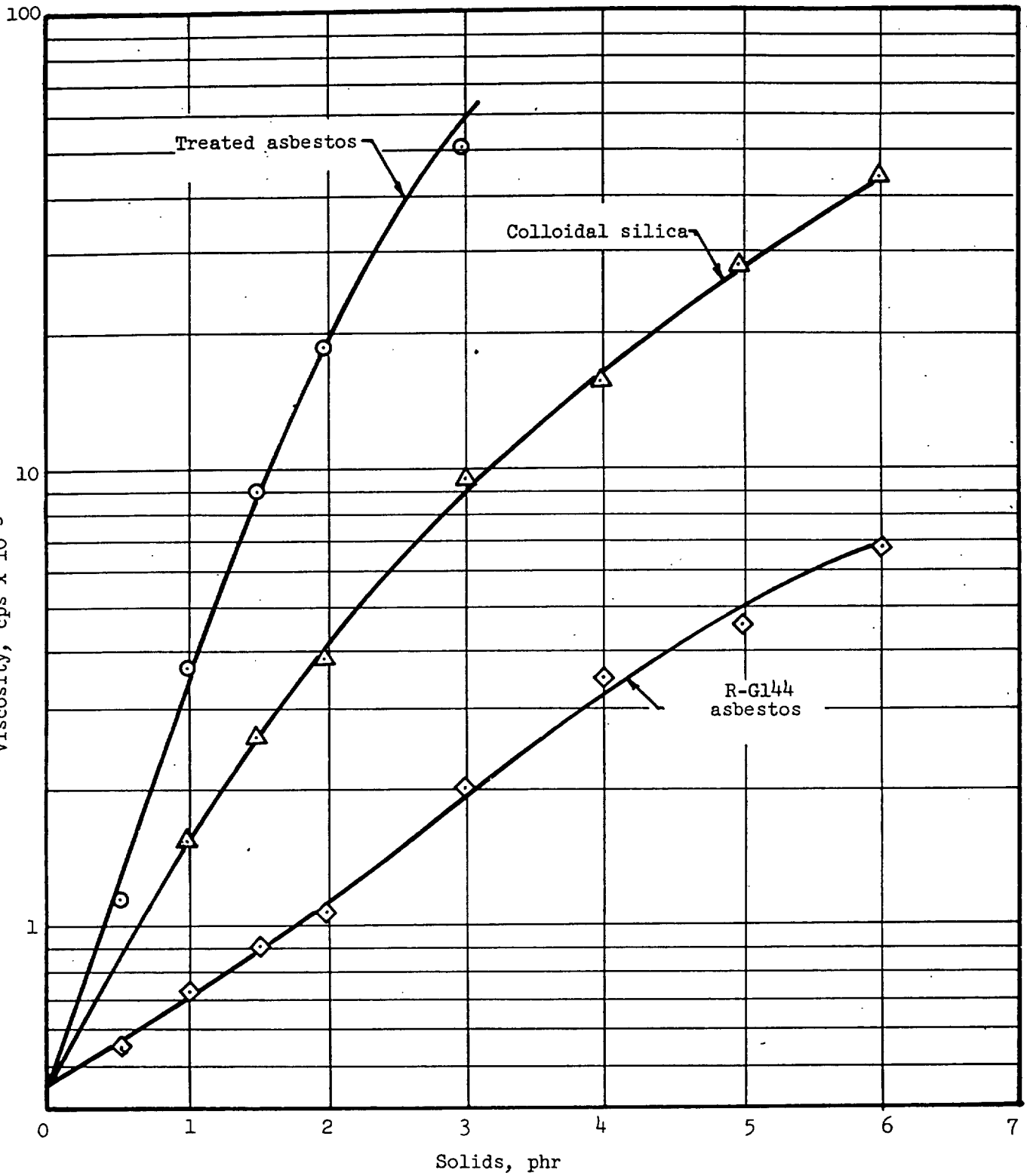


FIGURE 2 - VISCOSITY OF POLYESTER RESIN CONTAINING VARIOUS ADDITIONS OF PARTICULATE SOLIDS

Measurement - Spindle 4 at 12 rpm

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/11

3. Filtration by a Büchner filter, drying filter cake, and reopening the dried filter cake in a small Waring Blendor to form a fluffy powder

4. Evaluation of the effectiveness of the treatment by measuring the viscosity of the solids in polyester resin

The test resin used for evaluation was Rohm and Haas Paraplex P-43 diluted with enough styrene to reduce the initial viscosity to about 500 centipoise, as measured with a Brookfield LV Viscometer.

All viscosity measurements on suspensions which are reported without further qualifications have been determined by a Brookfield LV Viscometer with Spindle No. 4 at 6 rpm. The readings were taken after one minute. In the cases where T-bar spindles were used, a Helical Path attachment was used in conjunction with the Brookfield LV Viscometer. The criterion applied for the evaluation of the thickening power of treated asbestos was the value of the viscosity of the polyester resin containing 2 parts treated asbestos per 100 parts resin. A minimum specification of 20,000 cps was arbitrarily chosen as being acceptable, based on values obtained in initial tests. In later experiments, however, products were made readily which were at least twice as effective as thickeners for the polyester resin.

The detailed conditions and results of most of the tests are tabulated in the Appendix. The most significant data are presented in tables, or as graphs, in the main body of the report.

Conditions of Preparation

The effect of the pH of the treatment was studied systematically in five tests. In each test, sodium silicate solution was added slowly to a slurry of asbestos and simultaneously, enough acetic acid was added to maintain a given pH value. The quantities of reagents used in treating the asbestos are given in Appendix 1. The viscosities of the resulting solids in polyester are recorded in Appendix 1 also, and some of the data are plotted as a function of the pH of treatment in Figure 3(a). The filtrate solutions were analyzed and the recoveries of silica on the asbestos, calculated from the filtrate analyses, are shown in Figure 3(b). It is evident from these data that pH 8 is the best pH for treatment.

The amount of chrysotile in each product was determined from magnesium analyses, and the amount of silica in the chrysotile lattice was calculated by assuming that the normal chrysotile analysis is 41.5% MgO, 41.4% SiO_2. The remaining silica is designated as "free silica," and represents the amount placed on the asbestos by the treatment. The data are shown in Appendix 2. The silica recoveries calculated in this way are somewhat less than the amounts indicated from filtrate analyses, but they show the same pattern, i.e., best recovery of silica on the asbestos occurs at pH 8.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 12 of 49 asbestosclaims.law/library/16643/12

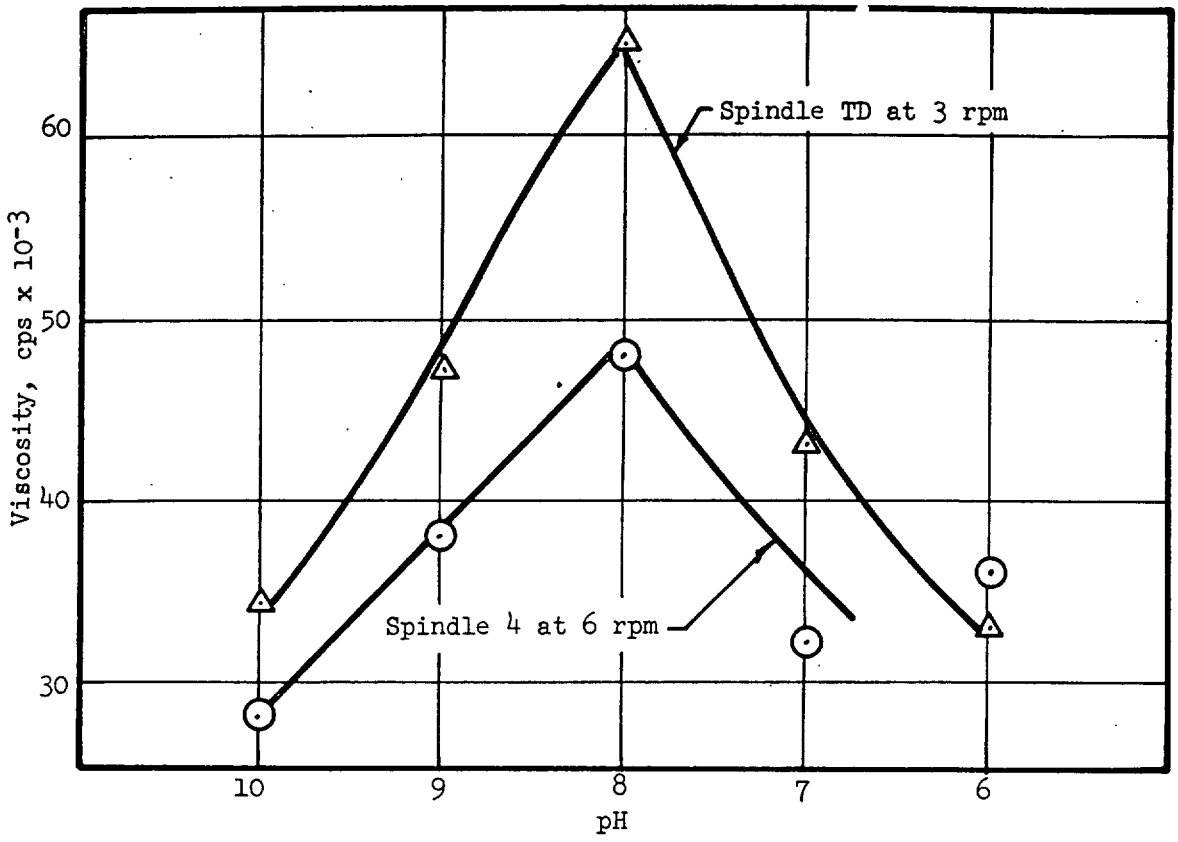


FIGURE 3(a) - THICKENING OF POLYESTER RESIN BY ASBESTOS TREATED WITH SILICA AT VARIOUS PH VALUES

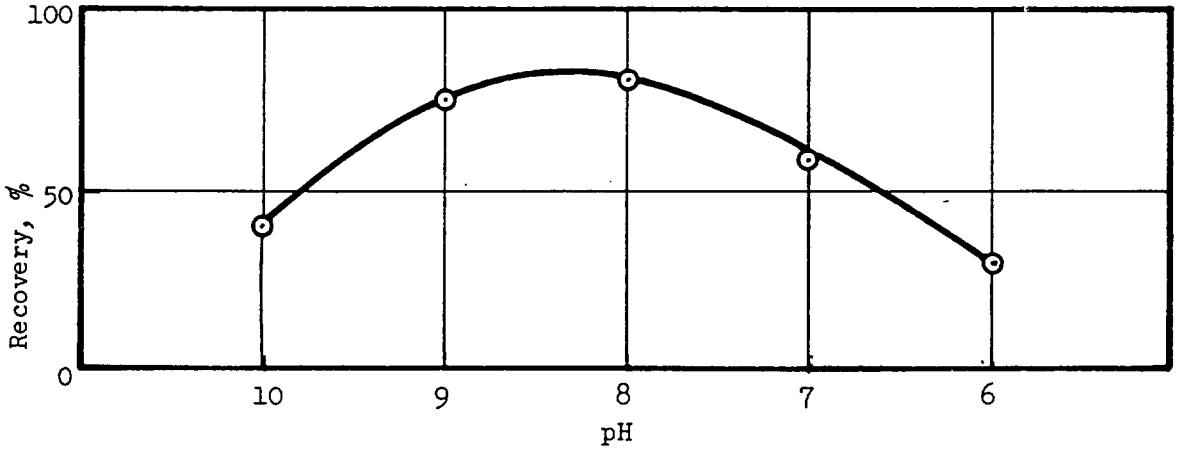


FIGURE 3(b) - RECOVERY OF SILICA ON ASBESTOS BY TREATMENT AT VARIOUS PH VALUES

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 13 of 49 asbestosclaims.law/library/16643/13

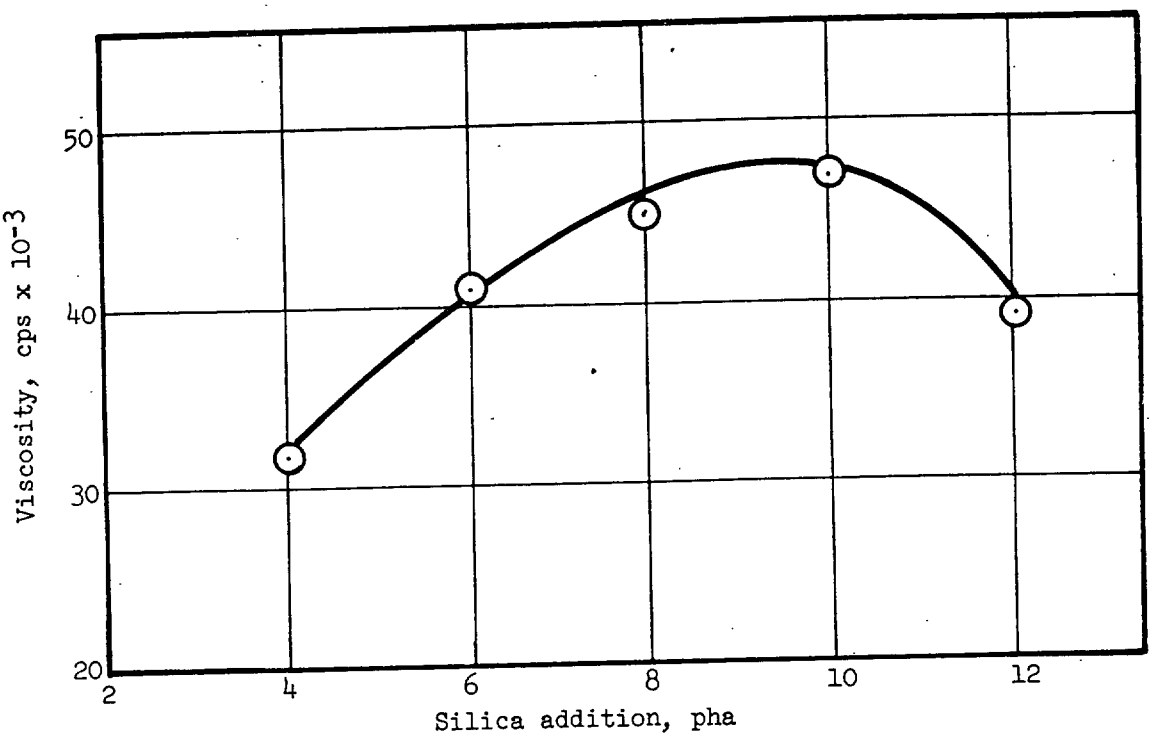


FIGURE 4(a) - THICKENING OF POLYESTER RESIN BY ASBESTOS TREATED AT PH 8 WITH DIFFERENT AMOUNTS OF SILICA

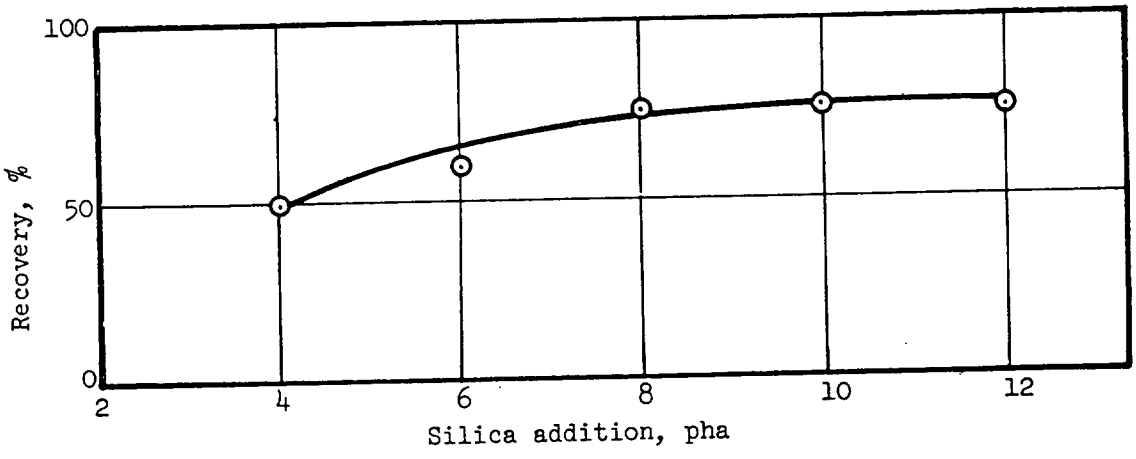


FIGURE 4(b) - RECOVERY OF SILICA ON ASBESTOS DURING TREATMENT AT PH 8 WITH DIFFERENT AMOUNTS OF SILICA

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 14 of 49 asbestosclaims.law/library/16643/14

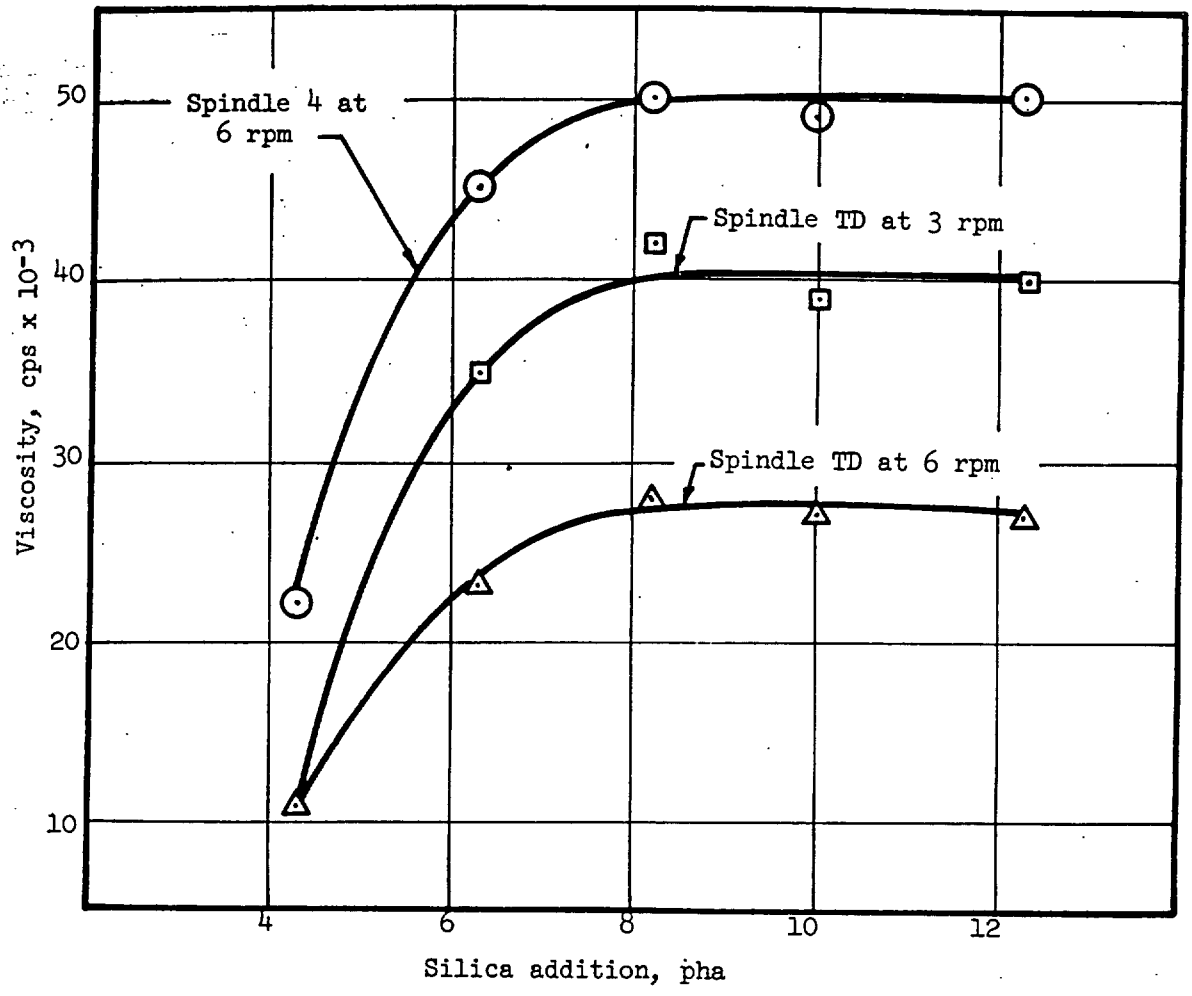


FIGURE 5(a) - THICKENING OF POLYESTER RESIN BY ASBESTOS TREATED WITH DIFFERENT AMOUNTS OF SILICA IN ACIDIFIED SUSPENSIONS

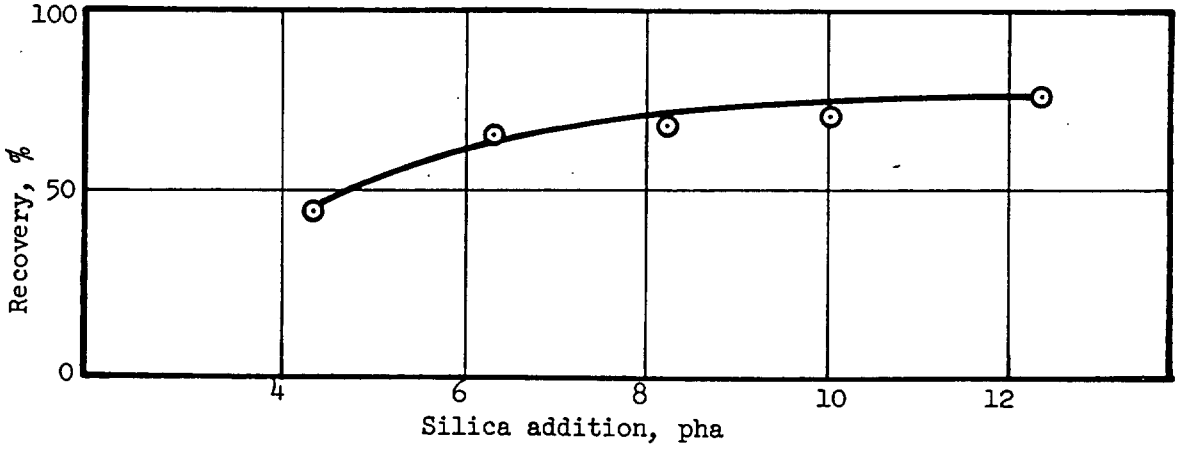


FIGURE 5(b) - RECOVERY OF SILICA ON ASBESTOS BY TREATMENT IN ACIDIFIED SUSPENSIONS

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/15



FIGURE 6 - REPLICA OF ASBESTOS FLAKE

Mag. 9000X, Photo No. 2949

material is desired. In spite of the relatively favorable opportunity for producing colloidal material from Coalinga chrysotile asbestos, the degree of liberation has caused some problems in laboratory work and a great deal of difficulty in pilot plant runs.

All of the asbestos used in our laboratory and in the pilot plant has been processed in our King City plant, so a satisfactory defibrilization has already taken place once. After opening and refining in the plant, the asbestos is filtered, pelletized, and dried. During these steps, enough strong reaggregation takes place so that most of the fibers become agglomerates, and significant amounts of energy are again required to liberate the fibers. In the laboratory, beating an aqueous suspension in a Waring Blendor at high speed for 3 minutes is satisfactory to liberate the fibrils in preparation for chemical treatment. In the pilot plant runs, it has been difficult to produce a well liberated slurry of asbestos. The King City plant production of this material will be easier, since the asbestos should be available as a slurry containing relatively well liberated fibrils. However, the associated problem of how to handle the treated asbestos (slurry) to produce a dried form which is readily dispersible may also be difficult to solve.

A number of experiments were done to study the effects of incomplete opening of the asbestos used for chemical treatment. Dry High Purity opened asbestos (pellets opened dry at King City) was used as the source of asbestos since this material was thought to be still weakly agglomerated. Charges of 2.5 liters of slurry containing 1% asbestos by weight were beaten in a large Waring Blendor for different lengths of time. Each was then given an identical chemical treatment - 50 milliters of 1 molar sodium silicate solution was added (12 pha of SiO_2) and the slurry was acidified to pH 8 with acetic acid. The treated asbestos was filtered, dried, and tested in polyester resin to evaluate its thickening power. Samples of the aqueous slurry in each test were taken before and after chemical treatment.

The conditions under which the tests were conducted are recorded in Appendix 7. The viscosities of the aqueous samples are given there also. No correlation was found between the viscosities of the aqueous samples and either (1) the amount of opening, or (2) the effectiveness of the treatment for polyester thickening. However, the untreated samples were also screened on a 10-micron sieve after dispersing with an anionic surfactant, Triton X-200. The amount retained on the screen was found to correlate roughly with the amount of beating of the asbestos slurry in the Waring Blendor. The data, tabulated in Appendix 7 and presented in Figure 7(a), show that after 3 minutes of thrashing in the Waring Blendor, only 4% of the weight of the asbestos was retained on the sieve. Data are presented in Figure 7(a) also which show that High Purity pellets opened under the same conditions are liberated substantially to the same degree. This screening procedure is the only means found to date that correlates with the degree of asbestos liberation. A specification of less than 4% by weight retained on the 10-micron sieve was tentatively suggested as the criterion for sufficient liberation of asbestos in preparation for silica treatment.

The treated asbestos from each test was mixed with polyester resin by an Eppenbach Homomixer for periods of 1 minute, 3 minutes, 5 minutes, and 10 minutes. The viscosities of the resulting suspensions are given in Appendix 8 and in Figure 7(b). As expected, the asbestos opened longer before treatment thickened the polyester better.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 17 of 49 asbestosclaims.law/library/16643/17

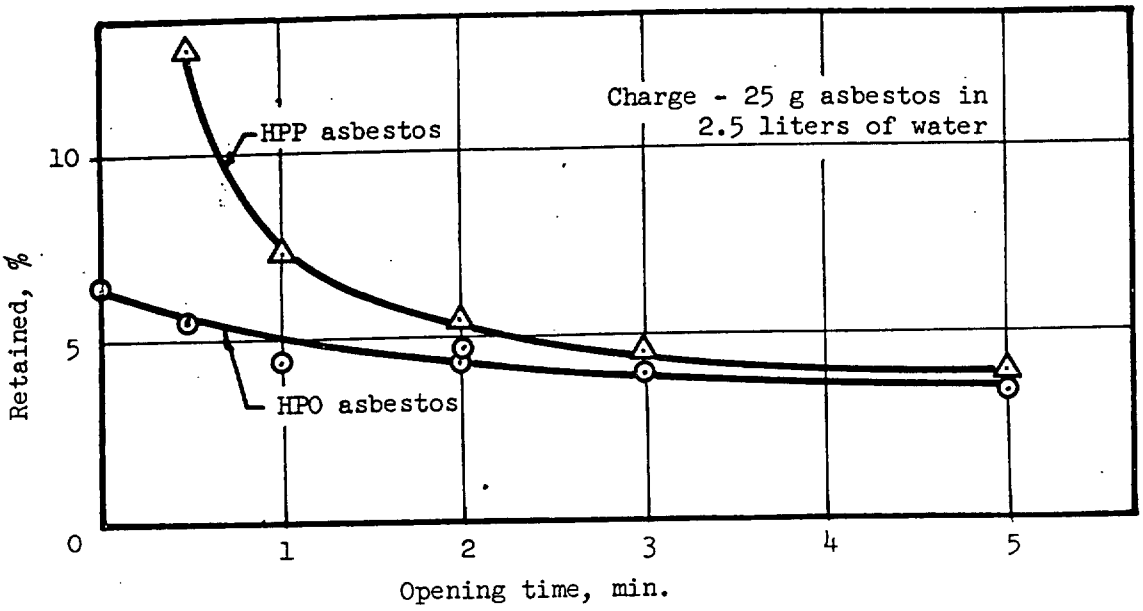


FIGURE 7(a) - RETENTION ON 10-MICRON SIEVE OF ASBESTOS OPENED IN A WARING BLENDOR

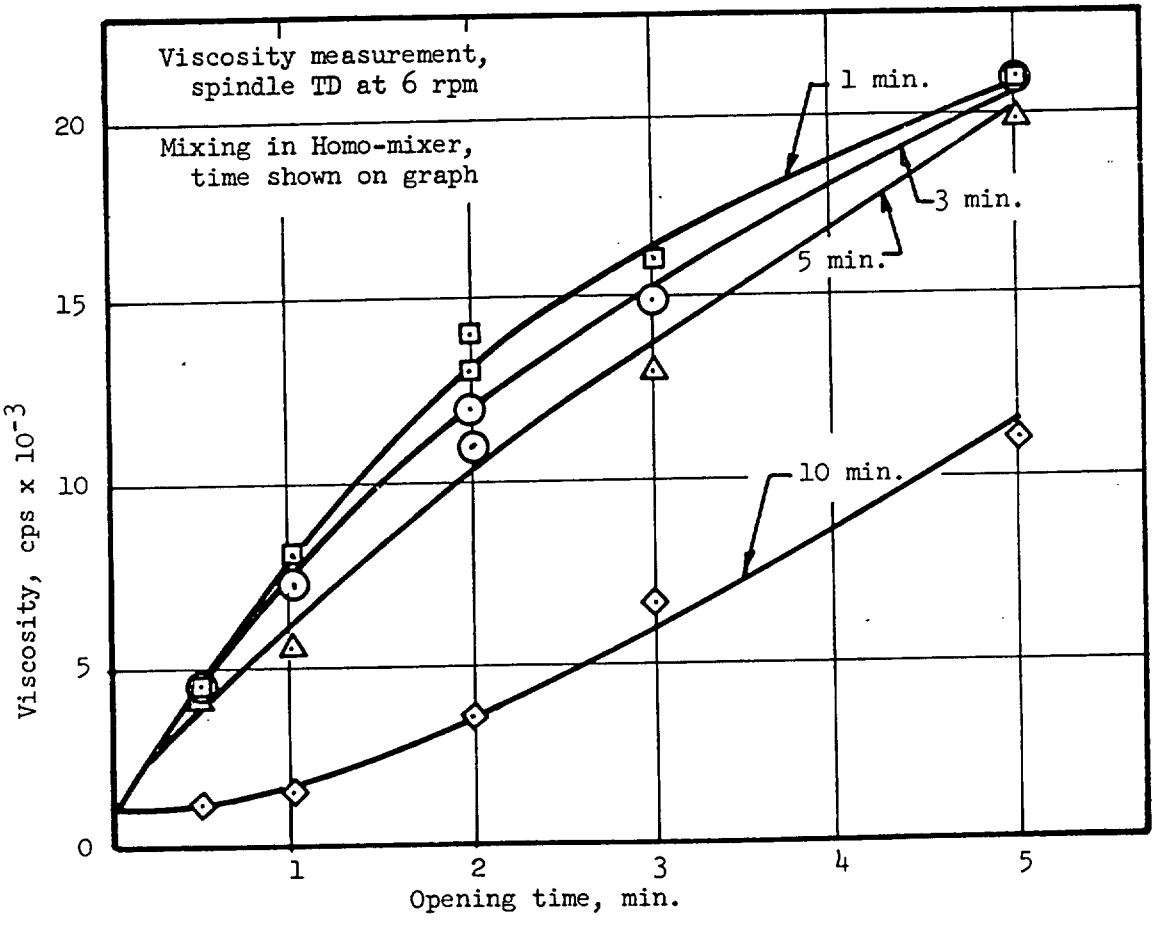


FIGURE 7(b) - EFFECT OF LIBERATION ON THICKENING OF POLYESTER RESIN BY SILICA-TREATED ASBESTOS

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso...
Published by AsbestosClaims.Law
ACL Doc 16643 · Page 18 of 49
asbestosclaims.law/library/16643/18

The effect of increasing the mixing time of the treated asbestos with the polyester from 1 minute to 5 minutes was to reduce the thickening power only slightly, but a large decrease in thickening was obtained after 10 minutes of mixing. Evidently, the shearing forces in the Homomixer are great enough to degrade the silica-treated asbestos after prolonged mixing.

The products from these tests were analyzed, and the results of calculations of silica recovery are reported in Appendix 9.

The effect of temperature on treatment was investigated. Experiments were done at 30°C. (nominal room temperature), 41°C., 51°C., and 61°C. in which sodium silicate and acetic acid were added simultaneously to maintain pH 8 in a 1% asbestos slurry. After addition of 12 pha of SiO_2, the slurry was filtered, dried, opened, and tested in polyester. Samples of both the solid and filtrate from each test were analyzed. The conditions and data are shown in Appendices 10 and 11. Some of the data are shown below in Table II. No advantage is seen in increasing the temperature of treatment from room temperature to 61°C.

TABLE II

Effect of Temperature on Silica Treatment of Asbestos

Temp. of treatment °C.	Viscosity in Polyester, cps x 10^{-3}
30 (room temp.)	48
41	40
51	43
61	31

Competitive Asbestos

Samples of competitive Coalinga and Canadian chrysotile and one of anthophyllite asbestos were tested as raw materials for a treated product. Table III shows the viscosities obtained in a polyester slurry at 2% solids before (control) and after silica treatment using our standard laboratory procedure. The data show both Canadian chrysotile and anthophyllite to be entirely unsuitable raw materaisl for this type of product. The Coalinga fiber, as represented by the two Atlas products, of course, is as good as our product after stringent hydraulic opening and could represent a competitive threat.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 19 of 49 asbestosclaims.law/library/16643/19

TABLE III

Silicate Treatment of
Competitive Asbestos Materials

	Viscosity in Polyester, cps x 10^{-3}	
	Control	Silica-Treated
Atlas AZ-20	1.3	89
New Atlas	1.6	76
Carey 7RF9	1.1	1.0
JM 7R06	-	2.5
Anthophyllite	0.5	0.6

Pilot Plant Production of Treated Asbestos

The responsibility for the transition of the process from the laboratory to the pilot plant was undertaken initially by Mr. J. L. Myers and then continued to completion by Mr. J. E. Skvarla.

After solution of the initial difficulty in producing a well liberated asbestos slurry for feed to the treatment process, treated asbestos which thickened polyester resin adequately (viscosity greater than 20,000 cps at 2 phr loading in the resin) could be made at will. Suitable feed was obtained by further opening of a slurry in a repulper and/or sizing in a 10-mm. cyclone. Some data relating the method of feed preparation and the results of treating the feed are shown in Table IV.

TABLE IV

Effect of Asbestos Liberation
During Silica Treatment in the Pilot Plant

Sample	Additional Opening	Additional Sizing	Viscosity in Polyester, cps x 10^{-3}
King City slurry	none	none	6
King City slurry	Waring Blendor	none	84
King City slurry	none	30-mm. cyclone	30
King City Slurry	none	10-mm. cyclone	72
High-purity pellets	Reitz mill		
	(a) 1 pass	none	29
	(b) 2nd pass	none	31
High-purity pellets	Reitz mill	30-mm. cyclone	28
High-purity pellets	Reitz mill	10-mm. cyclone	40

It is apparent that sufficiently liberated feed can be obtained by sizing the King City slurry with a 10-mm. cyclone or by further opening an asbestos slurry with a repulper.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 20 of 49 asbestosclaims.law/library/16643/20

A run was carried out to determine the effect of the pH of the silica treatment in the pilot plant. The feed to the run was sized, consecutively, in a 30-mm. cyclone and then in a 10-mm. cyclone. Sodium silicate was added to the slurry, and then the pH was reduced with acetic acid in stages. Samples were taken after each acid addition and tested for thickening power in polyester. The results are shown in Table V.

TABLE V

Effect of pH on Silica Treatment of Asbestos in the Pilot Plant

Test No.	pH	Viscosity in Polyester, cps x 10^{-3}
1684-26	10.2	8
	9.0	19
	8.0	28
	7.0	22
	6.0	26

These results support the laboratory tests which showed that pH 8 is optimum for treatment of the asbestos.

Pilot plant Run 59 (Reference 1684-63) was carried out, closely following the conditions recommended from the laboratory studies. A 4% aqueous slurry of asbestos was opened further in a Micro-pulverizer. This product was screened and found to contain less than 3% material retained on a 10-micron sieve. The slurry was divided into two parts.

For Run 59A, the sodium silicate was added first to one portion of the slurry at a treatment level of about 9 parts silica per 100 parts asbestos (9 pha), and then acetic acid was used to reduce the pH to 8. In Run 59B, the acetic acid was mixed with the other part of the slurry first, and then sodium silicate was added until a pH of 8 was reached.

The treated asbestos materials from each of these tests were equivalent in thickening power for polyester resin, as would be predicted from the laboratory tests.

A sample of Run 59A was studied in more detail. The variation in viscosity with different additions of the treated asbestos to polyester resin was measured. At the same time, similar data for Cab-O-Sil in polyester resin were obtained. Some of the results are shown in Figure 8, and all of the data are tabulated in Appendix 12. Previous data for thickening by untreated asbestos (HPO) are included in Figure 8 for comparison.

The surface charge characteristics of a dried sample of Run 59A are reported in a following section of this report entitled "Properties of Silica-Treated Asbestos."

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 21 of 49 asbestosclaims.law/library/16643/21

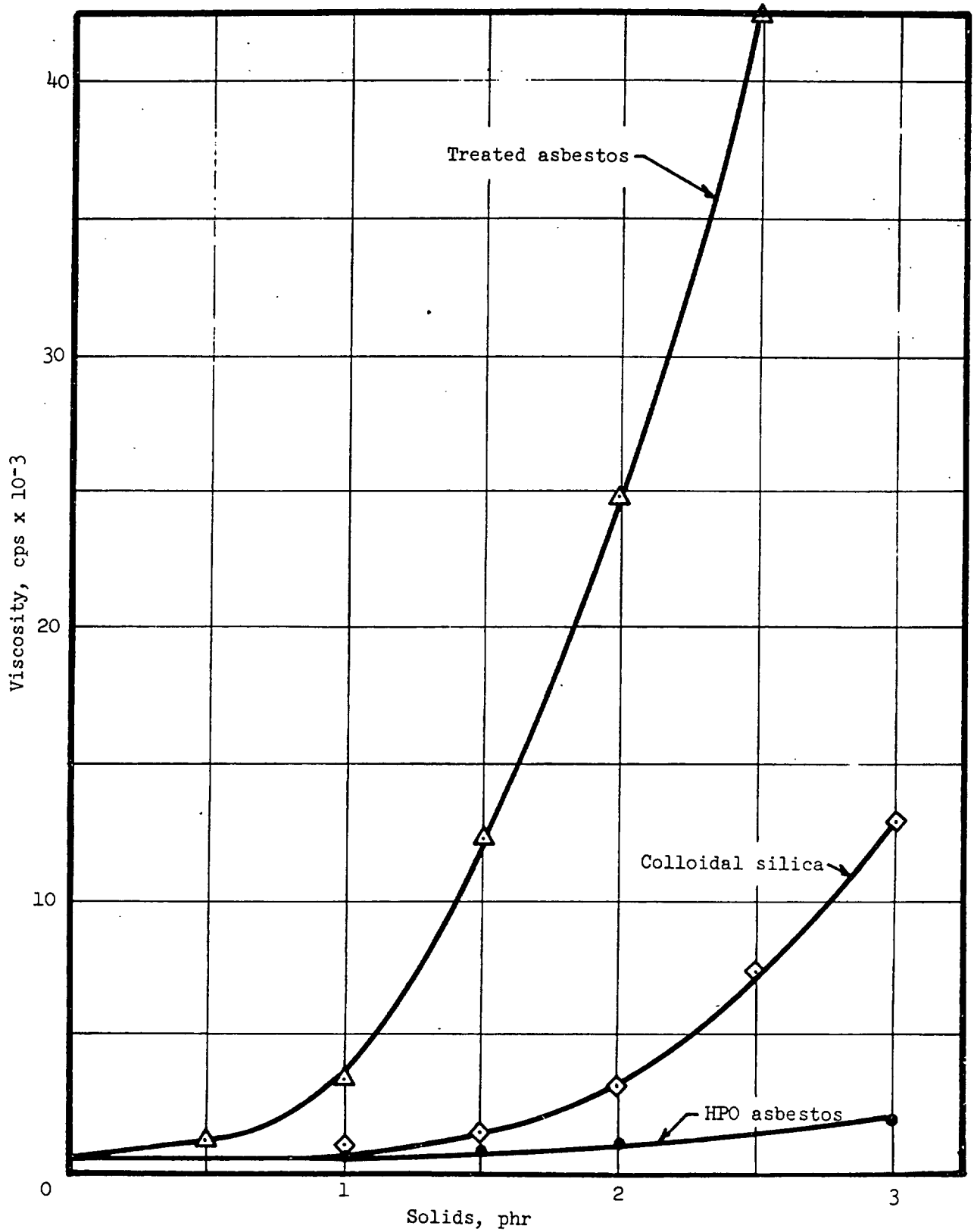


FIGURE 8 - COMPARISON OF THICKENING OF POLYESTER RESIN BY TREATED ASBESTOS FROM PILOT PLANT RUN 59A WITH COLLOIDAL SILICA AND WITH UNTREATED ASBESTOS

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 22 of 49 asbestosclaims.law/library/16643/22

Properties of Silica-Treated Asbestos

The most apparent effect of silica treatment is in the physical properties of the powder. The brightness, dry bulk, and wet bulk increase in comparison to untreated asbestos. The data are given in Table VI.

TABLE VI

Physical Properties of Asbestos, Treated Asbestos, and Cab-O-Sil

Property	Asbestos(1)	Silica-treated Asbestos	Cab-O-Sil
Brightness, %	·76	80-82	93
Dry Bulk(2), cc./g.	30	50	30
Wet Bulk(3), cc./g.	40-50	160	20

(1) High Purity pellets opened dry in a Waring Blendor

(2) 5 g. particulate solids opened dry in a Waring Blendor and allowed to settle in a 1-liter graduate

(3) 5 g. particulate solids opened dry in a Waring Blendor, mixed with one liter of water and allowed to settle in a 1-liter graduate

Silica treatment significantly changes the composition of the asbestos. Typical analyses for normal asbestos and for asbestos treated with 8 to 12 parts of silica per 100 parts of asbestos are shown below in Table VII.

TABLE VII

Typical Analyses of Silica-Treated Asbestos

Component	% Silica-treated Asbestos	% Asbestos
MgO	39-38	41.5
SiO_2	44-45	41.4
"Free" SiO_2	5- 7	0

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 23 of 49 asbestosclaims.law/library/16643/23

The product analyses in the preceding table represent recoveries of about 66-68% of the silica onto the asbestos surface. Calculations of recovery based on filtrate analyses indicate that the recoveries are somewhat higher - between 70 and 80% of the silica is calculated as being recovered on the asbestos. However, even if the latter figures are correct, the maximum amount of the "free silica" would be about 8%. If this silica occurred as a uniform coating on a fiber with a diameter of 250 Angstroms, it would have a thickness of about 10 to 15 Angstroms, depending on whether the density of the coating was that of pure silica or was somewhat less. A layer of this thickness would not be seen by normal examination under an electron microscope. Electron micrographs were made of an asbestos sample treated with 12 parts of silica per 100 parts of asbestos. Little incrustation can be seen on the fibers, so this reinforces the conclusion that most of the silica must be present as a very thin layer. The most obvious effect of the silica layer should be on the surface properties of the fibers.

The zeta potentials of asbestos products were measured on dilute suspensions by electrophoresis, and in some cases, by electro-osmosis through filter cakes of the solids. When the sign of the zeta potential is given without qualification, it may be assumed that the pH of the suspension measured was nearly neutral (pH 6 to 8). Chrysotile asbestos is normally positively charged, but the data in Table VIII show that its zeta potential becomes negative after treatment with 10 or more parts silica per 100 parts of asbestos. The zeta potential was observed to remain negative over a period of many weeks after silica treatment. Chemical analysis of the asbestos made in all tests by this treatment at these levels indicates that well opened asbestos has 5% to 6% "free" silica, or more, on its surface. Asbestos which is not as well liberated requires less silica to become negatively charged. However, it is evident from Table VIII that it is not necessary to obtain a negatively charged product to make a good thickener for polyester, but the conditions which in the extreme lead to the formation of a negative charge also result in an asbestos product which is an effective thickener for polyester resin. In fact, after filtering, drying, and reslurrying the dried solids in water, the zeta potential was found to be positive immediately in all tests. The reason for this charge reversal from negative to positive after drying is not known, but fortunately there was enough effect of the treatment left after drying so that the silica-treated asbestos remained a good thickener for polyester.

The effects of pH on the zeta potentials of a slurry sample of asbestos prepared in the pilot plant (Run 26, Reference 1684-25) and of a laboratory test No. 1708-99 are shown in Figure 9. Similar data, obtained on the dried silica-treated asbestos in another pilot plant test (Run 59A) are given for comparison. The latter material is still electropositive, although less than untreated asbestos. In contrast, the slurry samples of silica-treated asbestos are electronegative.

It is desirable to characterize the surface properties of the treated asbestos quantitatively by some means which is independent of its thickening properties for polyester. Accordingly, experiments to measure the adsorption of a cationic species on asbestos products were undertaken. Methylene blue cation was chosen for this purpose because it could be expected to show preference for negatively charged sites, and the analysis of methylene blue in solution was rapid and easy. However, previous data obtained by Dr. A. W. Naumann showed that some methylene blue adsorbed even on normal, positively charged asbestos.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 24 of 49 asbestosclaims.law/library/16643/24

TABLE VIII

Properties of Silica-Treated Asbestos

Test No. NB 1708	Opening Time, min.	pH of Treatment	Treatment Level, SiO_2 pha	Surface Charge Slurry	Surface Charge Dried	Visc. in Polyester cps x 10^{-3}	"Free" SiO_2 %	Rec.(1) SiO_2 %
44-1	3	8	12	(-)	(+)	39	6.6	75
44-2	3	8	10	(±)	(+)	47	5.5	75
44-3	3	8	8	(+)	(+)	45	3.3	74
45-1	3	8	6	(+)	(+)	41	1.1	60
45-2	3	8	4	(+)	(+)	32	1.7	49
28-1	0	8	12	(-)	(+)	0.9	4.4	65
28-2	0.5	8	12	(-)	(+)	6	6.5	71
28-3	1.0	8	12	(-)	(+)	12	5.7	80
29-1	2.0	8	12	(-)	(+)	12-21	6.7	74
30-1	2.0	8	12	(-)	(+)	20	6.8	73
29-2	3.0	8	12	(-)	(+)	25-36	5.8	75
29-3	5.0	8	12	(-)	(+)	46	6.5	78
96-1	3	9	12	(-)	(+)	50	7.6	80
96-2	3	9	10	(±)	(+)	46	5.9	71
96-3	3	9	8	(±)	(+)	45	4.9	70
96-4	3	9	6	(+)	(+)	37	3.2	64
96-5	3	9	4	(+)	(+)	17	1.7	53

(1) Recovery of SiO_2 on the solid is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 25 of 49 asbestosclaims.law/library/16643/25

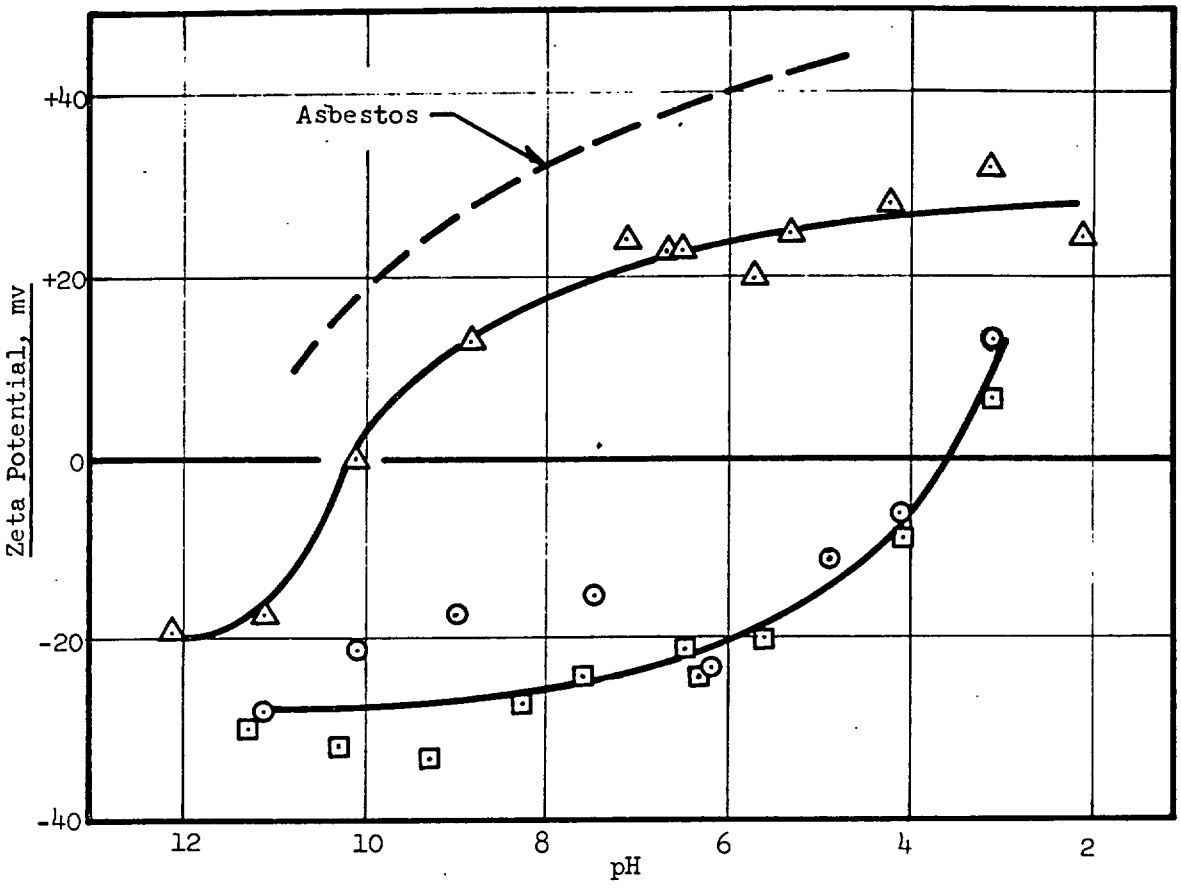


FIGURE 9 - ZETA POTENTIALS OF TREATED ASBESTOS SLURRY AND OF TREATED ASBESTOS AFTER DRYING

Description of Tests

Symbol	Preparation	Condition	Measurement	Analysis, % MgO	Analysis, % SiO_2	"Free" SiO_2, %
⊙ ⊙	Run 25	slurry	1685-67	37.0	46.1	9.2
△ △	Run 59A	dried	1708-89	41.2	44.5	3.4
⊡ ⊡	1708-99-1	slurry	1730-3	(~39)	(~45)	(~6)

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 26 of 49 asbestosclaims.law/library/16643/26

The experiments consisted of batch tests in which various amounts of methylene blue chloride solution (reagent grade) were mixed with suspensions of asbestos products in water. The suspensions were centrifuged and the clear solution analyzed for residual methylene blue. The amount adsorbed on the asbestos product was calculated as the difference between the amount of methylene blue chloride added to the system and the residual amount left in solution after adsorption. The asbestos products studied were: (1) silicate-treated asbestos in its treatment solution, (2) silica-treated asbestos which had been filtered, dried, and then reslurried in water, (3) normal High Purity Asbestos. The results are shown in Figure 10. The order of the magnitude of the maximum adsorption is the same as would be predicted from the electrophoresis data. The dried silica-treated asbestos adsorbs only about 20% more methylene blue than does the normal chrysotile, while the undried silica-treated asbestos, which is negatively charged, adsorbs twice as much methylene blue as the untreated chrysotile.

A possible interpretation of the data may be that even the positively charged asbestos has some negative sites, but that the silica treatment increases the number of these sites.

Although the quantity of methylene blue adsorbed on the various treated products is different, it was decided that the adsorption technique was unsuitable as a control test or as an evaluation means for the material produced by silica treatment. This conclusion was based on the fact that the rate of equilibration during the adsorption process was very slow. Often the equilibration continued for more than a day after an addition of methylene blue chloride to a suspension, which precludes the use of the technique for control or evaluation purposes.

The specific surface areas of a large number of treated asbestos products were determined by BET analysis of nitrogen adsorption data. The data were collected with a Perkins and Elmer Absorptometer.

The specific surface areas varied widely, but most of the values were in the range 50 to 55 $m.^2/g.$ Compared to a specific surface area of about 65 $m.^2/g.$ for untreated asbestos, the decrease in specific surface area is quite significant. The most likely explanation for this effect is that the asbestos was not fully liberated before treatment and that many aggregates of fibers were present. These aggregates are normally permeable to the nitrogen gas, but the silica treatment must have coated some of these aggregates, making them impermeable to nitrogen gas. This may be an explanation for the sensitivity of silica-treated asbestos to high shear stresses. For example, the coated asbestos aggregates could be broken up readily, exposing fibers with normal asbestos properties instead of the properties of silica-treated asbestos.

Mechanism of Silica Treatment

The highest treatment level recommended in this report, 12 parts silica per 100 parts asbestos, is achieved by mixing 50 ml. of 1 molar sodium silicate solution into 2.5 liters of suspension containing 25 grams of asbestos. The resulting pH of the suspension is about 12. The solution in the suspension contains 2×10^{-2} m./l. of sodium silicate at a pH of 12. From the data reported by Lagerstrom[2], it is evident that this solution is stable. When the pH is reduced to 8, however, the solution becomes supersaturated by a factor of 10 with respect to the formation of amorphous silica, i.e., solubility of silica is about 2×10^{-3} m./l. at pH 8.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 27 of 49 asbestosclaims.law/library/16643/27

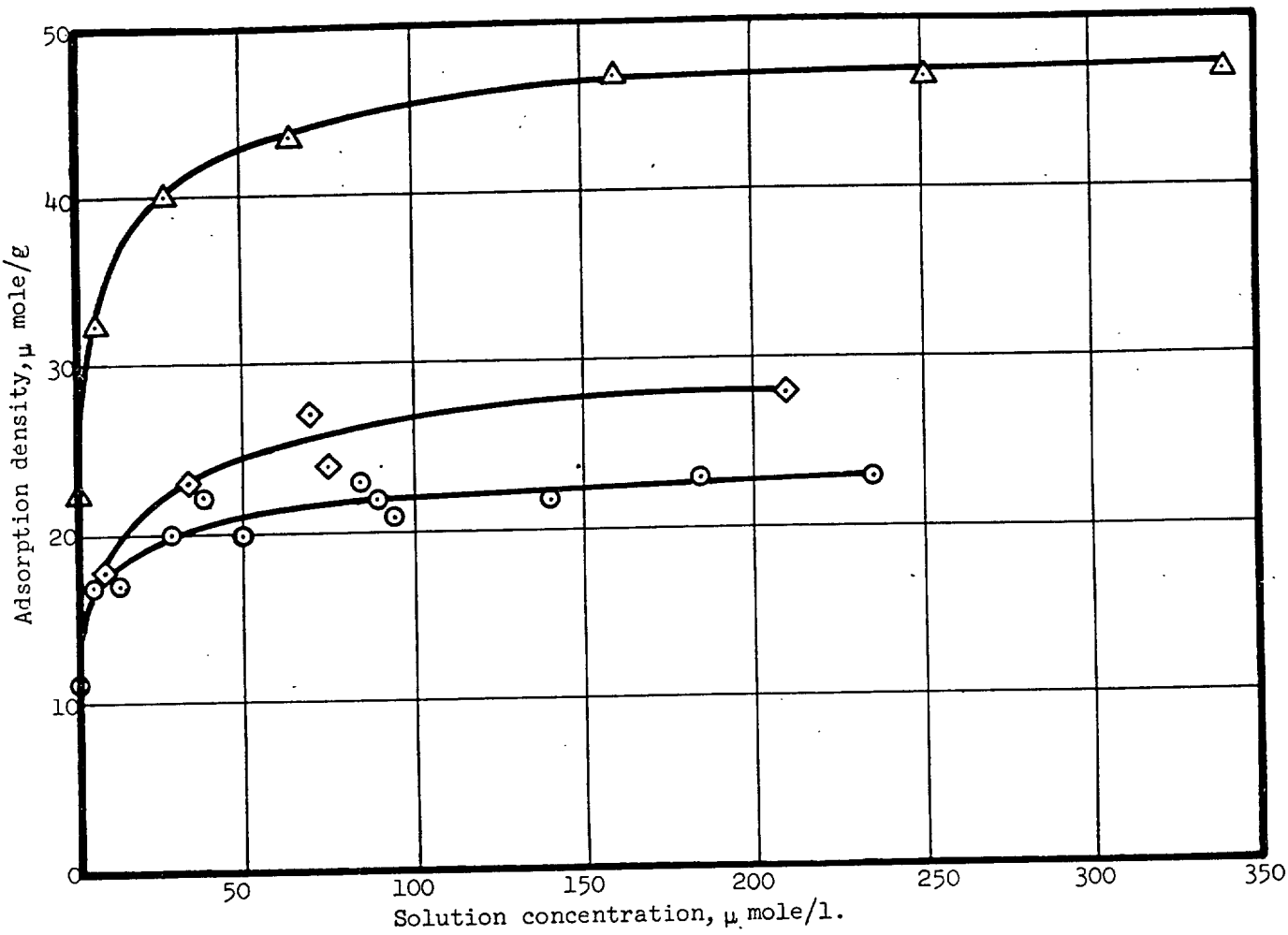


FIGURE 10 - ADSORPTION OF METHYLENE BLUE ON ASBESTOS PRODUCTS

Legend

Symbol	Product	Surface charge
△ △	silica-treated asbestos slurry	negative
◇ ◇	silica-treated asbestos	positive
⊙ ⊙	high-purity asbestos	positive

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso...
ACL Doc 16643 · Page 28 of 49
Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/28

The original mechanism proposed for silica treatment was that silica precipitates from solution, coating the asbestos in the suspension. A pure solution of sodium silicate under these conditions (2×10^{-2} moles per liter, pH 8) remains clear for long periods of time, exceeding the normal treatment time of about 10 to 30 minutes. This observation does not rule out the possibility of precipitation in an asbestos suspension, since the asbestos particles might act as nuclei for silica precipitation, but for analysis purposes, the whole process might conceivably be broken down into smaller steps. A system simulating adsorbed particulate silica on the asbestos was prepared by mixing Ludox (a fine colloidal dispersion of silica in water) with an asbestos suspension. The solids were filtered, dried, opened dry, and tested for their thickening effectiveness in polyester resin. While this material thickened polyester resin better than normal asbestos, it was not superior to the thickening power of Cab-O-Sil. Since silica-treated asbestos is much superior to Cab-O-Sil in thickening, the treated asbestos is evidently not just a mixture of asbestos and adsorbed particulate silica.

The preparation of a silica gel consists of changing the state of a sodium silicate solution so that it falls into an unstable (supersaturated) region of solubility. Silica polymers then form and slowly grow. When they become sufficiently long, the solution becomes turbid. After further growth, the silica polymers are long enough to overlap, and a solid gel forms.

Thus, a second possible mechanism is that silica polymers, which can be strongly negatively charged, adsorb on the asbestos surface. This mechanism was tested by treating asbestos with solutions containing polymerized silica species. It was predetermined that a 0.125 m./l. silicate solution at pH 8 became slightly turbid after 15 minutes of aging, indicating that some polymers had formed which were long enough to scatter significant amounts of light. With this knowledge, a series of tests were prepared to check the effect of pre-polymerized silica species on asbestos. Four solutions were prepared by diluting 50 ml. of 1 m./l. sodium silicate solution to 400 m./l. with distilled water, adjusting the pH to 8, and allowing the solutions to age for 1 minute, 5 minutes, 20 minutes, and 3 hours. The aged solutions were used to treat 2.5 liters of suspension (1% asbestos by weight), and the resulting solids were tested as thickeners for polyester resin. The results in Table IX show that a minimum of silica polymerization is desirable in the treatment solution.

TABLE IX

Polyester Thickening by Asbestos Treated with Aged Silica Solutions (Polymerized)

Test No. NB 1708	Aging Time min.	Silica Solution	Visc. in Polyester cps x 10^{-3}
93-1	~1	clear solution	42
54-1	5	" "	22
53-1	20	turbid "	12
56-1	180	gelled "	7

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 29 of 49 asbestosclaims.law/library/16643/29

Thus, the mechanism of silica treatment is most likely by adsorption of very short silica polymers or by adsorption of monomeric silica species followed by polymerization in-place on the asbestos surface. The thickness of the adsorbed layer of silica, estimated earlier in this report as 10-15 Angstroms, is such that a number of silica layers must form.

Mechanism of Thickening Polyester by Asbestos Products

The thickening of polyester resin by an asbestos product depends on two factors: 1) the nature of the reaction between the solid surface and components of the resin, and 2) the degree of interaction of the particles with each other. The predominant polyester resin used in our tests was Paraplex P-43, produced by Rohm and Haas, which had been diluted with about 10% additional styrene (final viscosity, approximately 500 cps.). The resin may be considered to be polyester polymers dissolved in a styrene solvent.

Based on visual observations, ordinary asbestos seems to be somewhat dispersed in the polyester resin, resulting in low-viscosity suspensions, while silica-treated asbestos appears to be flocculated in the resin, and its suspensions are much higher in viscosity. It was apparent that the difference in effect of the two solids depends on some specific reaction between one of the solids and the polyester resin.

Both asbestos and silica-treated asbestos thicken pure styrene liquid. This was expected since neither of these hydrophilic solids is compatible with the non-polar styrene liquid. Thus, most particles should interact on colliding, which would lead to a network of particles throughout the liquid. It was indeed found that a 1% suspension of either solid in the styrene has a Brookfield viscosity of about 5,000 cps under a given set of mixing conditions. When a 1% asbestos suspension is prepared in a 2:1 mixture of styrene and Paraplex P-43, the viscosity drops more than tenfold. However, the viscosity of a 1% suspension of silica-treated asbestos in the same styrene-Paraplex solution decreases to less than 1/2 of the viscosity in pure styrene.

The most likely explanation for this effect is that the polyester polymer adsorbs on the asbestos surface, causing "solvation" of the particle, which reduces the chances of a particle-particle interaction on collision. The silica sites on the silica-treated asbestos, however, do not seem to be affected by the polyester polymers, so enough particle-particle interactions take place to cause thickening of the polyester resin.

The nature of the reaction between the asbestos surface and the polyester polymers has not been studied. However, one would expect some reaction between the carboxylic acid group at the end of a polyester molecule with the basic magnesia groups found on the asbestos surface. In contrast, no reaction is likely between the polyester carboxylic acid group and the acidic sites on the silica-treated asbestos.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 30 of 49 asbestosclaims.law/library/16643/30

Product Utilization

R-G244 is ideally suited for viscosity control and thixotropy development in polyester resins. The resulting polyester thixotropes are water-clear and show little or no tendency for the R-G244 to settle. R-G244 shows no effect on the shelf life of the thixotropic resin mixture, except perhaps to improve it. Optical clarity is maintained up to 1% solids, and only a slight haze is observed up to 2%. Since the optimum viscosity range, from a viscosity standpoint, is below 10,000 cps (or below 1.5% by weight R-G244), this material should be useful in clear-gel coats and other applications where optical clarity can be exploited.

Figure 11 shows the relationship of viscosity to shear rate as measured with a Brookfield LV Viscometer. For comparative purposes, data have been included for a colloidal silica* product commonly used for viscosity control in polyester resins. It is obvious from the plot that R-G244 is more than twice as effective for viscosity build-up in the ranges shown. This is also apparent from the plot shown in Figure 2.

The data in Table X show the effect of high shear mixing over a period of time on the viscosity of R-G244 in a polyester system. These data indicate an optimum mixing time of 2 to 4 minutes on this type of equipment, which should be sufficient latitude for most applications.

The viscosities quoted were determined with a Brookfield LV Viscometer, using a No. 3 or 4 spindle at 6 rpm at a temperature of 25°C. The thixotropic nature of asbestos suspensions, however, makes for difficulty in obtaining reproducible values. Accordingly, an empirical technique for optimizing results was established, and all values quoted were obtained by this method unless otherwise noted. Using this technique, 10 individual viscosities, with an average value of 53,000 cps were determined to have a standard deviation of 6,000 cps. More reproducible viscosities often are obtainable using the Brookfield Helipath stand with T-bar spindles.

TABLE X

Effect of Mixing Time on
Treated Asbestos in Polyester Resin

Mixing, min.	Polyester Visc. cps x 10^{-3}
1	72
2	76
3	52
4	66
5	47
6	41
7	39
8	30
9	34
10	29

* CAB-O-SIL, M-5 (Godfrey Cabot Corporation)

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 31 of 49 asbestosclaims.law/library/16643/31

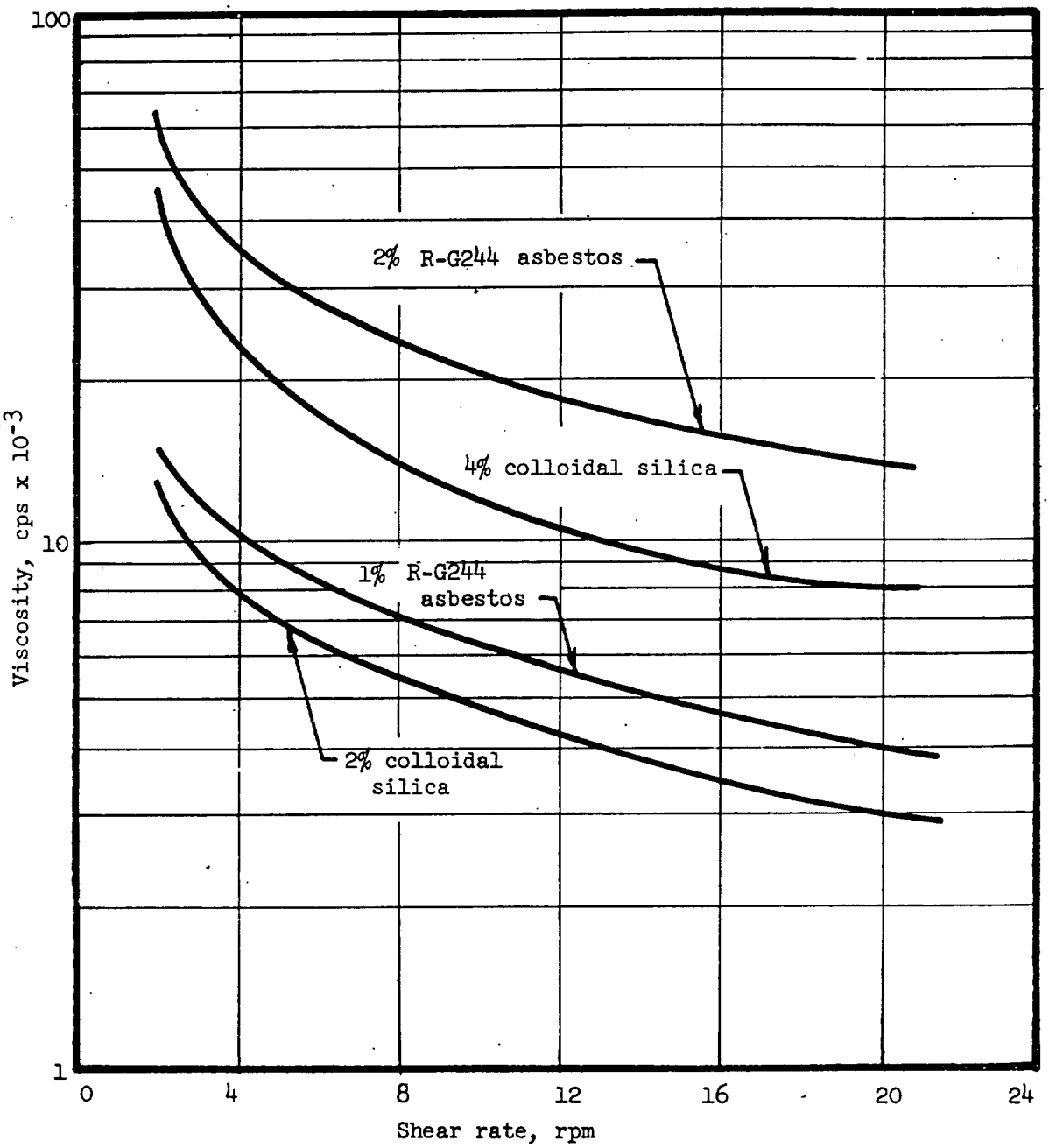


FIGURE 11 - EFFECT OF SHEAR RATE ON MEASURED VALUE OF APPARENT VISCOSITY OF POLYESTER SUSPENSIONS

Measurement - Brookfield LV Viscometer

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso… Published by AsbestosClaims.Law
ACL Doc 16643 · Page 32 of 49 asbestosclaims.law/library/16643/32

R-G244 may have some utility in other resin systems, both for viscosity control and as a reinforcing additive. These applications include viscosity control in plastisols and lattices and reinforcement of ABS and other sytrene-based polymers. They will be reported in subsequent reports.

Patent Position

A patent application has been made on the behalf of Union Carbide for the process and product described in this report(3).

A patent for a similar process is held by E. I. DuPont de Nemours & Company(4). It is entitled "Product Comprising a Skin of Dense, Hydrated Amorphous Silica Bound Upon a Core of Another Solid Material and Process of Making Same." One of the materials described as a suitable core for the silica skin was chrysotile asbestos. The temperature necessary for the described process is specified as between 60 and 125°C., and preferably between 80 and 100°C. Another condition that must be met is that the silica addition must not exceed the rate as calculated from a given equation. It is recommended in the patent that "the skin should for most purposes not be thinner than about 3 millimicrons (30 Å)."

It is apparent that none of these three basic conditions applies to our product or process as described in this report. Our process is best done at room temperature (30°), and there is no limitation on rate of addition of silica to our system. The resulting treated asbestos has a layer of silica on it which is less than 15 Å thick, and a layer of about 10 Å is probably sufficient. It seems that there should be no conflict with DuPont's patent. The latter patent also shows no proposed uses for their silica-treated products.

Avibest, a product of FMC Corporation, is presently being submitted to potential users for polyester thickening. This material has been described in various chemical news bulletins as a hydrated, polymeric, magnesium silicate, developed by Dr. O. A. Battista. It is reported that composition of matter, process, and application patents have been filed for Avibest, but only European patent lists have carried summaries of the descriptions and claims for the product. From the literature released by FMC, their process consists of attacking chrysotile asbestos with strong hydrochloric acid solutions, probably at slightly elevated temperatures, and then subjecting the asbestos to "intense mechanical agitation to release some 10 to 15% of the material as rod-like microcrystals averaging about 200 Å in diameter and 5000 Å long." From this description, it appears that the starting asbestos source for FMC's process is probably cross fiber asbestos, as mined in Quebec, which is much more difficult to liberate than is Coalinga asbestos. Avibest was studied in our laboratories and found to be suitable for thickening polyester resins. Its composition was found to be deficient in magnesia(5), as would be expected after an acid treatment. It is probably the silica-rich characteristic of the surface, formed by leaching, which makes the Avibest suitable as a thickener for polyester. This acid leaching process was also studied in our laboratory, but it was rejected in favor of silica treatment due to the difficulty in controlling the degree of acid leaching and the further difficulty of removing the dissolution products by filtration. It is the authors' opinion that FMC's process is both costly and difficult to control.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 33 of 49 asbestosclaims.law/library/16643/33

CONCLUSIONS

From this work, the following conclusions may be drawn:

1. A superior thixotropic additive for polyester resins can be made by silica treatment of UCC chrysotile asbestos.

2. A silica treatment with 8 to 10 parts silica per 100 parts of the asbestos produces the optimum product.

3. The most critical step in the manufacture of this product is the preparation of a well liberated, colloidal asbestos fiber.

4. Conventional Grade 7 Canadian chrysotile cannot be silica treated to produce an equivalent product.

5. Acceptable product has been produced in pilot plant equipment using the laboratory conditions presented.

R. E. Byrne, Jr.

S. Chwastiak

REB/SC:et
Attach.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 34 of 49 asbestosclaims.law/library/16643/34

APPENDIX 1

Silica Treatment of Asbestos at Various pH Values

Test No. NB 1685	pH of Treatment	Reagents(1) Sod. Silicate m. moles	Reagents(1) Acetic acid m. moles(2)	Viscosity in Polyester cps x 10^{-3} Spindle 4 3 rpm	Spindle 4 6 rpm	Spindle 4 30 rpm	Spindle TD 6 rpm	Spindle TD 3 rpm	Thixotropic Index(3)
92-3	10.0	50	72	45	28	13	20	34	3.5
91-1	9.0	50	76	57	38	16	30	47	3.6
91-2	8.0	50	75	66	48	>20	>33	65	-
92-1	7.0	50	100	48	32	14	26	43	3.4
92-2	6.0	50	106	55	36	14	20	33	3.9

(1) Added to a 1% aqueous slurry containing 25 g. asbestos.

(2) Excludes the acid required for pH adjustment before the sodium silicate is added.

(3) Thixotropic Index calculated as ratio of apparent viscosities at 3 rpm and 30 rpm, measured with Spindle 4.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 35 of 49 asbestosclaims.law/library/16643/35

APPENDIX 2

Analyses of Products from Silica Treatment at Various pH Values

Test No. NB 1685	pH of Treatment	Filtrate Analysis SiO_2, g./l.	Solid Analysis, %			Calculations, %		
			Brightness	MgO	SiO_2	"Free" SiO_2 (1)	Rec. of SiO_2 (2)	Rec. of SiO_2 (3)
92-3	10	0.69	82	39.51	42.84	3.4	32	40
91-1	9	0.26	81	37.90	45.00	7.2	67	77
91-2	8	0.21	80	37.90	45.08	7.3	68	81
92-1	7	0.47	81	38.78	44.76	6.0	56	59
92-2	6	0.79	81	39.84	42.92	3.1	29	30

(1) "Free" SiO_2 is calculated as the difference between the total SiO_2 assay of the product and the amount of silica in the asbestos lattice itself, assuming an analysis of 41.5% MgO, 41.4% SiO_2 for the asbestos.

(2) Recovery of SiO_2 on the solid is based on the amount of "free" SiO_2 present on the solid compared to the addition of silica to the system.

(3) Recovery of SiO_2 on the solid is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 36 of 49 asbestosclaims.law/library/16643/36

APPENDIX 3

Silica Treatment of Asbestos at pH 8 with Different Amounts of Sodium Silicate

Test No. NB 1708	Nominal Addition of SiO_2 pha[1]	Reagents[2]		Viscosity in Polyester, cps x 10^{-3}		
		Sod. Silicate m. moles	Acetic acid m. moles	Spindle 4 6 rpm	Spindle TD 3 rpm	Spindle TD 6 rpm
45-2	4	17	30	32	15	12
45-1	6	25	44	41	25	18
44-3	8	33	59	45	39	24
44-2	10	42	74	47	47	26
44-1	12	50	86	39	27	18

(1) Parts per hundred parts of asbestos

(2) Added simultaneously to a 1% aqueous suspension, containing 25 g. asbestos, so that a constant pH of 8 was maintained.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso...
ACL Doc 16643 · Page 37 of 49
Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/37

APPENDIX 4

Analyses of Products from Silica Treatment of Asbestos Made with Different Additions of Sodium Silicate

Test No. NB 1708	Addition of SiO_2 pha	Filtrate Analysis SiO_2, g./l.	Solid Analysis, %			Calculations, %		
			MgO	SiO_2	Brightness	"Free" SiO_2	Rec. of SiO_2 (1)	Rec. of SiO_2 (2)
45-2	4	0.21	40.55	42.20	80.0	1.7	44	49
45-1	6	0.24	40.34	41.40	81.0	1.1	19	60
44-3	8	0.21	39.66	42.88	82.0	3.3	45	74
44-2	10	0.25	38.61	44.04	81.5	5.5	60	75
44-1	12	0.30	38.33	44.92	80.5	6.6	62	75

(1) Recovery of SiO_2 on the solid is based on the amount of "free" SiO_2 present on the solid compared to the addition of silica to the system.

(2) Recovery of SiO_2 on the solid is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 38 of 49 asbestosclaims.law/library/16643/38

APPENDIX 5

Silica Treatment of Acidified Asbestos Suspensions with Different Amounts of Sodium Silicate

Test No. NB 1708	Nominal Addition of SiO_2 pha	Reagents and Conditions (1)				Viscosity in Polyester, cps x 10^{-3}		
		Acetic acid		Sodium Silicate		Spindle 4	Spindle TD	
		m. moles	pH	m. moles	pH	6 rpm	3 rpm	6 rpm
64-1	12.3	95	3.5	51.5	8.2	50	40	27
64-2	10.0	80	3.5	41.7	8.0	49	39	27
64-3	8.2	65	3.5	34.4	8.1	50	42	28
66-1	6.3	50	3.6	26.2	8.1	45	35	23
66-3	4.3	35	3.8	17.5	8.1	22	~ 9	~11

(1) Enough sodium silicate added to a 1% aqueous suspension (acidified), containing 25 g. asbestos, so that a final pH of 8 was obtained.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 39 of 49 **asbestosclaims.law/library/16643/39**

APPENDIX 6

Analyses of Products from Silica Treatment of Acidified Asbestos Suspensions Made with Different Additions of Sodium Silicate

Test No. NB 1708	Nominal Addition of SiO_2 pha	Filtrate Analysis SiO_2, g./l.	Solid Analysis, % MgO	Solid Analysis, % SiO_2	Calculations, % "Free" SiO_2	Calculations, % Rec. of SiO_2 (1)	Calculations, % Rec. of SiO_2 (2)
64-1	12.3	0.28	38.38	45.70	7.4	68	77
64-2	10.0	0.30	37.83	44.56	6.8	75	70
64-3	8.2	0.26	39.97	44.04	4.1	54	68
66-1	6.3	0.21	39.57	43.20	3.7	63	66
66-2	4.3	0.23	41.03	42.40	1.4	34	45

(1) Recovery of SiO_2 on the solid is based on the amount of "free" SiO_2 present on the solid compared to the addition of silica to the system.

(2) Recovery of SiO_2 on the solid is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 40 of 49 asbestosclaims.law/library/16643/40

APPENDIX 7

Silica Treatment of HPO Asbestos Opened Further in a Waring Blendor

Test No. NB 1708	Asbestos Suspension (1%)(1) Opening Time(2) min.	Retained on 10-micron sieve, %(3)	Visc. in Polyester cps x 10^{-3}	Reagents and Conditions Sod. Silicate m. moles	Acetic Acid m. moles	Final pH	Treated Asbestos Suspension (1%) Visc. in Polyester cps x 10^{-3}
28-1	0	6.7	(settles)	50	85	8.1	(settles)
28-2	0.5	5.6	10-11	50	86	8.0	17-20
28-3	1.0	4.5	10	50	85	8.1	25-29
29-1	2.0	4.8	12-13	50	90	7.6	21-24
30-1	2.0	4.4	13-14	50	87	8.2	26-28
29-2	3.0	4.0	13-14	50	86	8.1	20-23
29-3	5.0	3.4	11-12	50	88	8.1	37-40

(1) Starting suspension, 2.6 l. containing 26 g. HPO asbestos.

(2) Suspension thrashed at high speed in large Waring Blendor.

(3) 100 ml. of opened asbestos suspension withdrawn for sizing on a 10-micron sieve.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 41 of 49 asbestosclaims.law/library/16643/41

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso...
ACL Doc 16643 · Page 42 of 49

APPENDIX 8

Thickening of Polyester by Silica-Treated HPO Asbestos Opened Further in a Waring Blendor

Viscosity in Polyester after Various Mixing Times,(1) cps x 10^{-3}

Sample No. NB 1708	Opening Time, min.	1 min. mixing				3 min. mixing				5 min. mixing				10 min. mixing		
		Spindle 4 at 6 rpm	Spindle TD 6 rpm	Spindle TD 0.6 rpm	T.I.(2)	Spindle 4 at 6 rpm	Spindle TD 6 rpm	Spindle TD 0.6 rpm	T.I.(2)	Spindle 4 at 6 rpm	Spindle TD 6 rpm	Spindle TD 0.6 rpm	T.I.(2)	Spindle 4 at 6 rpm	Spindle TD 6 rpm	Spindle TD 3 rpm
28-1	0	~1	~1	~1	-	~1	~1	~1	-	~1	~1	~1	-	~1	~1	~1
28-2	0.5	9.5	4.3	12	2.8	6.0	4.5	12	2.8	5.5	4.0	13	3.2	1.5	1.2	~1
28-3	1.0	14	8.0	32	4.0	12	7.2	32	4.4	12	5.5	22	4.0	2.0	1.5	1.7
29-1	2.0	23	14	55	3.9	31	12	50	4.2	22	11	42	3.8	7.0	3.5	3.3
30-1	2.0	26	13	53	4.1	20	11	48	4.4	23	11	47	4.3			
29-2	3.0	39	16	75	4.7	25	15	62	4.1	35	13	53	4.1	14	6.6	6.0
29-3	5.0	38	21	93	4.4	48	21	77	3.7	54	20	73	3.6	32	11	14

(1) 2 parts silica-treated asbestos and 100 parts polyester mixed in an Eppenbach Homomixer for various lengths of time.

(2) T.I. - Thixotropic Index, ratio of apparent viscosity at 0.6 rpm to apparent viscosity at 6 rpm.

Published by AsbestosClaims.Law
asbestosclaims.law/library/16643/42

APPENDIX 9

Analyses of Products from Silica Treating HPO Asbestos Opened Further in a Waring Blendor

Test No. NB 1708	Opening Time, min.	Filtrate Analysis SiO_2, g./l.	Solid Analyses, %			Calculations, %		
			MgO	SiO_2	Brightness	"Free" SiO_2	Rec. of SiO_2 (1)	Rec. of SiO_2 (2)
28-1	0	0.42	40.07	44.42	76	4.4	41	65
28-2	0.5	0.35	37.82	44.34	80	6.5	61	71
28-3	1.0	0.24	39.59	45.08	80	5.7	53	80
29-1	2.0	0.31	38.62	45.22	81	6.7	62	74
30-1	2.0	0.32	37.90	44.60	82	6.8	63	73
29-2	3.0	0.29	39.43	45.08	82	5.8	54	75
29-3	5.0	0.27	37.58	44.36	82	6.5	61	78

(1) Recovery of SiO_2 on the solid is based on the amount of "free" SiO_2 present on the solid compared to the addition of silica to the system.

(2) Recovery of SiO_2 on the solid is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 43 of 49 asbestosclaims.law/library/16643/43

APPENDIX 10

Effect of Temperature on Silica Treatment of Asbestos

Test No. NB 1685	Temp. °C.	Reagents(1) Sod. Silicate m. moles	Reagents(1) Acetic acid m. moles	Viscosity in Polyester cps x 10-3 Spindle 4 3 rpm	Spindle 4 6 rpm	Spindle 4 30 rpm	TD 6 rpm	T.I.(2)
91-2	30	50	75	66	48	>20	>33	-
98-1	41	50	94	66	40	14	33	4.7
98-2	51	50	95	70	43	16	33	4.4
98-3	61	50	95	48	31	12	22	4.0

(1) Added to 2.5 l. of aqueous suspension containing 25 g. asbestos, pH kept constant at 8.

(2) T.I. - Thixotropic Index, the ratio of apparent viscosity at 3 rpm to apparent viscosity at 30 rpm.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 44 of 49 asbestosclaims.law/library/16643/44

APPENDIX 11

Analyses of Products from Silica Treatment of Asbestos at Different Temperatures

Test No. NB 1685	Temp. °C.	Filtrate Analysis SiO_2, g./l.	Solid Analysis, %			Calculations, %		
			MgO	SiO_2	Brightness	"Free" SiO_2	Rec. of SiO_2 (1)	Rec. of SiO_2 (2)
91-2	30	0.21	37.90	45.08	80	7.3	68	81
98-1	41	0.28	37.74	45.40	81	7.6	71	77
98-2	51	0.30	37.74	45.20	82	7.6	71	75
98-3	61	0.28	37.58	45.72	81	7.3	68	77

(1) Recovery of SiO_2 on the solid is based on the amount of "free" SiO_2 present on the solid compared to the addition of silica to the system.

(2) Recovery of SiO_2 on the solid is based on the difference between the addition of SiO_2 to the slurry and the amount of SiO_2 discarded in the filtrate.

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 45 of 49 asbestosclaims.law/library/16643/45

APPENDIX 12

Thickening of Polyester by Pilot Plant Product from Run 59A

Reference	Addition to Polyester, phr(1)	Viscosity in Polyester, cps x 10^{-3}					
		Spindle TD		Spindle 4		Spindle 3	
		6 rpm	3 rpm	6 rpm	60 rpm	6 rpm	60 rpm
NB 1708, pages 86 and 88	0	0.5	0.5	0.5	0.5	0.5	0.5
	0.5	1.2	1.3	1.2	1.0	1.1	0.9
	1.0	2.8	3.1	3.5	1.9	3.2	1.7
	1.5	7.9	10	12	3.6	12	>2
	2.0	14	18	25	6.1	-	-
	2.5	22	30	42	9.5	-	-
	3.0	33	51	64	>10	-	-

(1) phr - parts per 100 parts of resin

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 46 of 49 asbestosclaims.law/library/16643/46

APPENDIX 13

Thickening of Polyester by Cab-O-Sil, Reference, NB 1708, pp. 84-85

Addition to Polyester, phr	Viscosity in Polyester, cps x 10^{-3}							
	Spindle TD		Spindle TB		Spindle 4		Spindle 3	
	6 rpm	3 rpm	6 rpm	3 rpm	6 rpm	60 rpm	6 rpm	60 rpm
0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
0.5	0.7	0.7	0.61	0.61	0.7	-	0.60	0.61
1.0	0.8	0.8	0.73	0.76	0.9	-	0.88	0.89
1.5	1.1	1.3	0.93	0.93	1.6	1.5	1.8	1.3
2.0	1.7	1.7	1.2	1.2	3.2	2.0	2.9	1.8
2.5	3.3	3.3	1.8	1.8	7.6	2.8	-	-
3.0	7.8	9.3	4.0	4.2	13	3.7	-	-

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 47 of 49 asbestosclaims.law/library/16643/47

REFERENCES

(1) E. Martinez and G. L. Zucker, "Asbestos Ore Body Minerals Studied by Zeta Potential Measurements," Journal of Physical Chemistry, 59 (1955) 892-895

(2) G. Lagerström, "Equilibrium Studies of Polyanions III. Silicate Ions in $NaClO_4$ Medium," Acta Chemica Scandinavica, 13 (1959) 722-736

(3) U.S. Patent Application No. 589,116, "Asbestos Composition," by S. Chwastiak, assigned to Union Carbide Corporation, D-6678, P.M. 0973

(4) U.S. Patent Serial No. 2,885,366, dated May 5, 1959, "Product Comprising a Skin of Dense, Hydrated Amorphous Silica Bound Upon a Core of Another Solid Material and Process of Making Same," by R. K. Iler, assigned to E. I. DuPont de Nemours and Company

(5) S. Chwastiak, "Avibest, An Asbestos Product of F.M.C. Corporation," memorandum to Mr. H. F. Reichard, Research and Development Department, Mining and Metals Division, Niagara Falls, N. Y., dated June 20, 1966

Union Carbide trial exhibit UC-1541: R. E. Byrne, Jr. and S. Chwastiak, The Chemical Modification of UCC Chryso... Published by AsbestosClaims.Law
ACL Doc 16643 · Page 48 of 49 **asbestosclaims.law/library/16643/48**

DISTRIBUTION

BOUND BROOK

I. Allen
W. T. Higgins
W. Miller
P. E. Pratt
R. W. Quarles
P. A. Thomas
N. L. Zutty

NEW YORK

F. D. Dexter
L. P. Jehle
A. E. Pufahl
N. J. Setter
L. Shechter
J. Sidlovsky
J. F. Voit
J. R. Wilkinson

SOUTH CHARLESTON

J. W. Biddle ✓
F. B. Brown
N. R. Eldred
R. I. Hoaglin
F. Johnston
C. S. Maxwell
C. W. McGary
J. J. Smith
F. J. Welch

TARRYTOWN

T. H. Welch

BRUSSELS, BELGIUM

T. J. Hall

KING CITY

J. A. Riddle +
J. L. Myers

NIAGARA FALLS

W. H. Blackwell
G. L. Dickson
R. A. Hard
B. L. Ingalls
M. S. Kisiel
E. J. Markiewicz
K. Park
J. E. Skvarla
F. H. Thompson
R. G. Woolery

TONAWANDA

S. Sterman