THE REINFORCEMENT OF POLYMERIC STRUCTURES BY ASBESTOS FIBRILS

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The Final Report, covering the period April 1, 1965 to April 30, 1966, was inadvertently submitted without Figures 1 and 2. Enclosed is the page with the missing Figures 1 and 2, which should be attached to the Final Report.

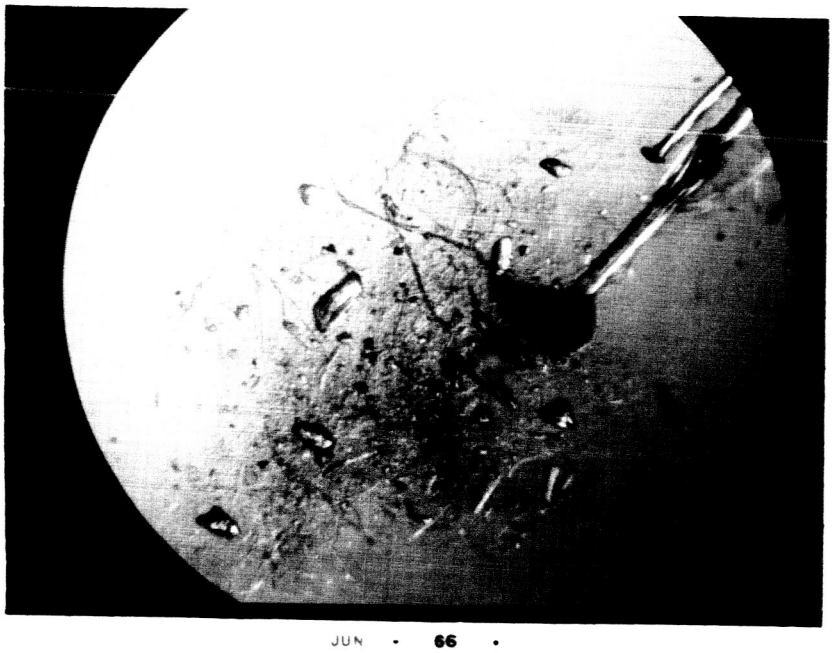

Figure 1. Photomicrograph of stirred asbestos dispersion in Aerosol OT solution.

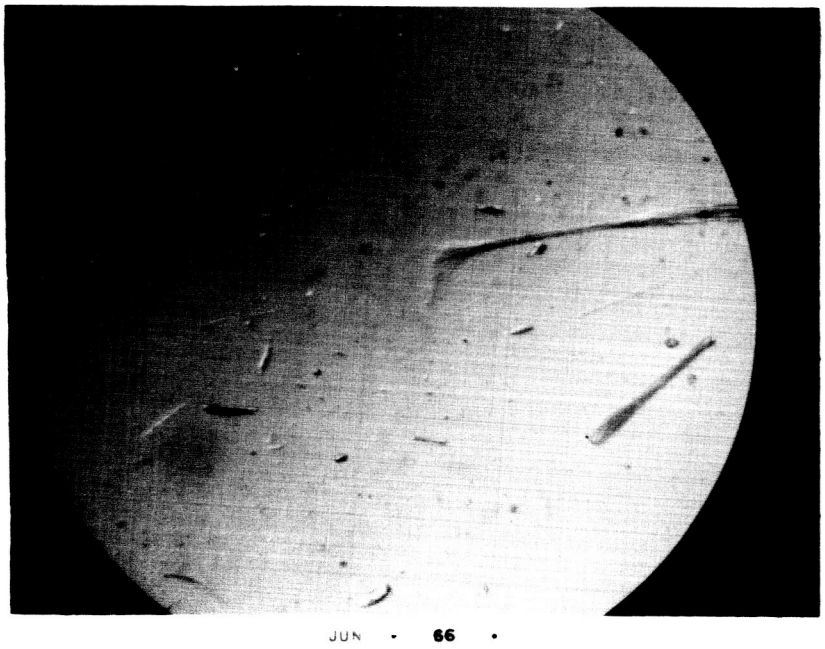

Figure 2. Photomicrograph of 6 minute Osterized dipsersion of asbestos in Aerosol OT solution. Longest MF splint is 375 microns in length and 8 microns in diameter.

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SUMMARY

This program has been concerned with the reinforcement of polymeric structures by ultimate asbestos fibrils (abbreviated UAF) having diameters in the range of 250 to 500 Angstroms. Techniques have been worked out for (1) dispersing conventional asbestos fibers into these extremely fine UAF, (2) incorporating the UAF as reinforcements in polymeric matrixes, and (3) forming sheet-form composites suitable for tensile testing. Novel dispersing techniques were discovered which enabled the dispersion to UAF to be carried out directly in organic solvents for the matrix resins, or in liquid, monomeric, resin precursors. Composites were also prepared from novel types of aqueous dispersions of UAF in which water-soluble resin precursors were employed as the dispersants.

Papers of all UAF, not containing resin, were found to be several-fold stronger than a commercial paper comprising mixed UAF and macroscopic asbestos fibers (MF), despite the fact that the commercial paper was made from oriented fibrers whereas the UAF papers prepared were isotropic. The UAF displayed a reinforcing effect in a variety of polymeric matrixes. However, the resin-containing composites reinforced solely by UAF (isotropic) were not significantly stronger, on a psi basis, than composites reinforced by the oriented MF/UAF mixed fibers of the commercial paper.

Composites containing up to 20% surfactant deposited on the UAF were equal or greater in strength than composites containing no surfactant.

In the UAF-reinforced composites tensile strengths were found to be roughly proportional to the length-to-diameter ratios of the fibrils.

I. INTRODUCTION

The primary objective of this program has been to determine the structural potential of asbestos fibrils employed as reinforcements in polymeric matrixes. The use of ultimate asbestos fibrils (UAF) of 250-500 Angstrom diameter has been emphasized in this program because of the expected strength advantages of UAF over conventional macroscopic asbestos fibers (MF). The MF, whose diameters range up to 100 microns or more, are actually very tight agglomerates of UAF bonded laterally by weak crystal forces. On a psi basis the flawless UAF should be superior to the MF agglomerates. Work under this program has been directed toward realizing this potential strength advantage of UAF in asbestos/polymer composite structures. In approaching the problem of UAF reinforcement work has been conducted in the two task areas specified in the contract "statement of work" as follows:

"1. Fibril Dispersion Processes - Hydrophilic and hydrophobic dispersion processes shall be investigated to determine the following:

a. The processes which yield the most practical specimens for determination of physical properties.

b. Processes which appear to yield higher physical properties when combined as composites.

2. Determination of Structural Potential - Analytical and experimental methods shall be used to explore the potential for asbestos fibrils as structural materials and shall include the following:

a. Potential maximum usable physical properties.

b. Forms and conditions for fibrils and fibril composites which will develop full potential.

c. Problem areas which need solution prior to achieving item a."

This Final Report Summarizes the work done in the one year contract period.

II. DISCUSSION

The determination of the structural potential of asbestos fibrils relies on the preparation and testing of suitable composites, i.e., composites which will yield meaningful test data in regard to their physical properties. In attempting to produce suitable UAF-reinforced composites three major problem areas are encountered, each having an important bearing on the performance of the final composite. In broad terms these three basic problems are: (1) attainment of complete conversion of MF to UAF, (2) attainment of good adhesion between the UAF and the matrix material, and (3) attainment of a well-engineered, void-free composite in which the UAF and matrix are not segregated. These are discussed below.

(1) In attaining complete conversion of MF to UAF we have found that, by selecting the proper dispersing technique and the proper dispersing medium for the asbestos, UAF can be produced in a range of length-to-diameter ratios. Since the UAF in Chrysotile asbestos have fairly uniform diameters, in the range of 250-500 Angstroms, the only geometric variable is the fibril length. We have explored a number of dispersing techniques and employed a variety of dispersing media in order to obtain UAF in a range of lengths. We have ascertained by light microscopy if the dispersions were free of large MF splints (over about 2 microns diameter) and ascertained in a single series of electron microscope observations if complete dispersion to UAF was achieved. The length and diameter of the UAF have also been determined using the electron microscope.

Novak teaches in U. S. Patent 2,626,213 that asbestos can be dispersed to UAF by prolonged stirring in selected aqueous surfactant solutions. We have noted that dispersions prepared by Novak's method contain much MF in addition to the UAF and the surfactant. We have filtered dispersions of this type to remove the large MF and obtained the UAF fraction in the filtrate. The colloidal UAF have then been collected by coagulation, either by adding alcohol or by adding enough water to reduce the surfactant concentration

below the level needed to stabilize the colloidal suspension. A portion of these UAF are extremely long (in comparison to their diameter) as evidenced by the fact that they readily spin onto a stirring rod twirled in the coagulated suspension.

We have found that ball milling of MF in aqueous surfactant solutions produces dispersions somewhat similar to the stirred dispersions. Like the stirred dispersions, both MF and UAF are present and filtration and coagulation can be used to collect the UAF.

We have also obtained UAF by extensively milling MF/surfactant dispersions with high shear (e.g. in an Osterizer). This technique is more rapid and thorough than the slow, Novak-type stirring or ball milling and essentially 100% dispersion to UAF can be achieved. However, the UAF obtained this way are shorter than the UAF recovered from ball-milled or Novak-stirred asbestos. This is evidenced qualitatively by the fact that no "spinnable" UAF is present.

In addition to the aqueous surfactant solutions we have discovered a second type of dispersing medium for asbestos. We have found that certain organic liquids effectively disintegrate asbestos to UAF when suitable agitation is employed. The organic liquids employed appear to be less efficient dispersers than the better surfactant solutions. However, with high speed shearing essentially 100% dispersion to UAF has been achieved. Although the UAF tend to be shorter than those obtained with surfactant dispersants (and, indeed, no spinnable UAF has been obtained from the organic liquid dispersions), these organic media have several valuable attributes. First, the volatile organics (glycols, amines) can be completely removed from the UAF by evaporation, leaving no residue. Second, the organic media

can serve as solvents for a matrix resin thus allowing an intimate mixing of the resin with dispersed UAF before removing the solvent in forming the final desired composite. Third, the organic media can serve as precursors or components of the matrix resin. For example, we have dispersed MF to UAF in linoleic acid and directly formed composites with good strengths by heat-curing the mixtures to polymerize the linoleic acid.

A novel method of mixing UAF and monomeric resin precursors has also been developed. In this method we have converted the monomer to a soap (e.g. linoleic acid, ammonium or morpholine soap) and used an aqueous solutiontion of this soap as the dispersing medium for asbestos. Thus, as the asbestos is dispersed to UAF, it is intimately covered with a deposit of the reactive dispersant. Composites are then readily formed by removing the water and volatilizing the basic group (ammonia or morpholine). The final composite produced is an intimate mixture of UAF and monomer which can then be cured to polymerize the monomer in situ. Advantages of this technique are that the UAF/matrix ratios can be carefully controlled and the water medium can be readily removed.

We have employed the UAF obtained by the different techniques as reinforcements in various resin matrixes. We have found generally that the longer (spinnable) UAF tend to promote higher strength composites than the shorter (non-spinnable) UAF. Our longest UAF, however, do not appear to be any better in reinforcing than some of the unfractionated MF/UAF mixtures of approximately equal fiber length. As a point of comparison we have used commercially available Novabestos paper (a product of Raybestos-Manhattan Corp.), impregnating this with resins to form composites. The Novabestos paper, which is made from an unfractionated

Novak-type dispersion, contains both MF and UAF oriented by the paper-making process. The Novabestos paper also contains about 5% of the dispersant, oleate soap. Although our UAF-reinforced composites were no stronger than Novabestos-reinforced composites, it should be kept in mind that our UAF was not oriented and did not contain the oleate soap. Further, before resin-impregnation, some of our UAF papers (despite their isotropy) were three times as strong as Novabestos paper in its strongest (oriented) direction.

(2) The attainment of good adhesion between UAF and the matrix material depends not only on the selection of suitable matrixes which bond strongly to the UAF, but also on the surface state of the UAF. Since the UAF can be obtained as pure asbestos (from dispersions in volatile organic liquids) or with a surface coating of surfactant or conditioning agent, it is necessary to determine what condition of the UAF is needed to achieve good bonding with the selected matrix.

When UAF dispersions made with Aerosol OT (or other surfactant) solutions are filtered or coagulated, the fibrils recovered contain a high proportion of adsorbed surfactant. If the whole dispersion is evaporated to form a paper, the proportion of surfactant is even higher (and is known precisely without having to analyze). In either case this adsorbed residual surfactant must profoundly affect the bonding of the UAF to any matrix material that may be used. In the special case where we employ a matrix precursor as our dispersing surfactant we expect that good UAF-matrix bonding should be realized. We have investigated the effect of residual surfactant with selected matrix resins. In much of this work we have elected to use the types of resins which have been found suitable for reinforcement

with MF, namely: phenolics, silicones, and polyesters. We have found that the presence of as much as 20% Aerosol OT surfactant has no significant effect on the strengths of UAF-reinforced phenolic or polyester composites. With our silicone resin (DC 1107), we have found that a small amount of surfactant is actually needed to effect adequate resin curing. There appears to be a specificity in the UAF conditioning for the silicone composites since the silicone does not cure on pure asbestos or on UAF which have been treated with a silane coupler of the type used in glass fiber-reinforced composites.

(3) Regarding their geometry, the UAF-reinforced composites we have prepared and studied have all been in the form of sheets or films on the order of a few mils thickness. No attempt has been made to orient the reinforcing fibrils and we have found no evidence of anisotropy. Commercially available Novabestos paper, which is produced on standard paper-making equipment from a Novak-type dispersion of MF and UAF in sodium oleate solution, is anisotropic. When tested untreated or as a reinforcement for a phenolic resin it is two to three times as strong in its machine (oriented) direction as in its cross-machine direction. Our best UAF-reinforced composites have exhibited equal, bidirectional strengths intermediate between the two extremes of Novabestos. It should be kept in mind again, however, that our UAF did not contain the deposit of oleate soap which is present on Novabestos.

For high strength we obviously desire solid, void-free composites containing uniformly distributed reinforcing fibrils. We have been most successful in eliminating voids by pressing the papers at 400 to 1000 psi. Where composites have been made from preformed asbestos papers we have used vacuum impregnation to fill the papers' voids with resin (in solvent)

followed by pressing to compensate for void volume created by solvent evaporation. It has been difficult to get solid isotropic composites having relatively high proportions of UAF because the randomly oriented fibrils resist being compressed into a tight structure, and relatively high proportions of resin have been needed to fill the inter-fibril spaces. Theoretically, cylindrical asbestos fibrils, when perfectly oriented, should pack to a structure having only 9.3% voids and a density of 2.27 g/cc. Our best solid isotropic composites, to date, have densities of 1.7 g/cc and contain only about 55% asbestos.

The colloidal nature of UAF makes it difficult to get even distribution of asbestos in the composite. The UAF exhibit typical colloidal behavior in tending to flocculate or agglomerate and, indeed, we use this property to fractionate dispersions and obtain the long, spinnable UAF. We have seen undesirable examples of coagulation when adding polyvinyl alcohol to aqueous surfactant dispersions of UAF. The papers cast from these dispersions show segregated areas relatively rich or poor in asbestos. Segregation can be minimized in this system by first making the UAF/surfactant paper and, subsequent to drying, impregnating the paper with polyvinyl alcohol solution. Where we have used a resin precursor as the dispersing surfactant (e.g. basic soap of linoleic acid), we have found that segregation is minimized if we can evaporate off the water first, leaving soap and UAF, and then evaporating off the base to get the desired composite. Thus morpholine linoleate has been found preferred over ammonium linoleate because morpholine is less volatile than ammonia and does not as readily evaporate at the same time as the water. In reducing segregation in composites prepared from UAF/resin dispersions in organic solvent media, we have been most successful by removing the majority of the dispersing medium by

filtration and then evaporating off the small amount of solvent which remains. Evaporation of large quantities of solvent tends to promote resin migration and segregation in the composite.

Our experimental program has been carried out with cognizance of the three problem areas discussed above. Because of the interdependency of so many of the variables, a large number of experiments have been conducted in order to evaluate the contribution of each variable to the overall problem of UAF reinforcement.

III. EXPERIMENTAL AND RESULTS

A. Dispersing Techniques

Throughout the early stages of this program we employed two types of dispersing techniques for converting MF to UAF. These were (1) stirring in surfactant solution (as taught in Novak's patent) and (2) shear-mixing at high speed (in an Osterizer). The stirred dispersions were always found to contain much undispersed MF along with the UAF, even after 24 hours stirring. The Osterized dispersions were found to contain little or no MF if carried out for a sufficient period of time, usually 60 minutes or more. Shorter mixing times resulted in dispersions containing higher proportions of MF. It was noted in our 3rd Quarterly Report that composites reinforced with mixed MF/UAF (6 minutes Osterizing) were stronger than comparable composites reinforced with 100% UAF (90 minutes Osterizing). None of our MF/UAF was as strong as comparable Novabestos composites, however, as shown in Table 1. It was considered that this may have been due to the much higher surfactant content of our papers compared with the surfactant content of Novabestos and/or due to the high content of macro-

TABLE 1. Comparison of Novabestos and Aerosol OT-Asbestos Composites

Paper	Resin	Paper Composition				Properties			
		Resin wt. %	Aerosol OT wt. %	Asbestos wt. %	Oleate Soap wt. %	Thickness mils	Density g/cc	Elongation %	Tensile Strength[4] psi
Novabestos[3]	None	0	0	94.5	5.5	3.4	0.57	7	520
MF/UAF[1]	None	0	32	68	0	7.8	1.1	2	820
UAF[2]	None	0	32	68	0	7.1	1.2	1	610
Novabestos[3]	Phenolic	46	0	51	3	2.8	1.4	2	13900
MF/UAF[1]	Phenolic	53	15	32	0	9.9	1.5	3	4600
UAF[2]	Phenolic	53	15	32	0	8.5	1.4	2	2100
Novabestos[3]	Polyester	44	0	52.9	3.1	3.0	1.4	3	14400
MF/UAF[1]	Polyester	47	17	36	0	10.0	1.5	4	5700
UAF[2]	Polyester	47	17	36	0	10.4	1.4	4	2600

1) Obtained by 6 minutes in the Osterizer.

2) Obtained by 90 minutes in the Osterizer.

3) The Novabestos was used as received, containing about 5.5% oleate soap.

4) Refer to page 10 for a discussion of how tensile strength is calculated.

scopically long MF in Novabestos. Our Osterized dispersions of MF/UAF contain only about 20% MF by weight; Novabestos has a much higher MF content. It should be kept in mind that the tensile strength data in this Table (as well as in Tables 2-7) are calculated on the basis of the actual composite thicknesses, as measured with a micrometer. No correction has been made for the void space which in some instances is as high as 80%. The reported strength is based on Instron tensile tests of one-half inch wide samples, initially one inch long (distance between Instron jaws). Thus a simple correction for void space would increase the reported strength values accordingly.

This correction has not been made because the effect of the voids may actually be more profound, particularly if the voids act as crack-starting flaws. Since we are not able to evaluate this effect, we have elected to report the tensile strengths, as measured, for the void-containing composites, as prepared. Figures 1 and 2 show, respectively, typical asbestos dispersions produced by stirring and 6 minutes Osterizing. These photomicrographs are chosen to show the same weight of asbestos. UAF is not visible in these photos, taken through a conventional light microscope. We have ascertained by microscopic examination, and by fractionation and weighing, that stirring converts only about 10% of the asbestos to UAF while 6 minutes Osterizing converts about 80% of the asbestos to UAF. The relatively very low MF content of 6 minute-Osterized dispersions is clearly demonstrated in Figure 2. We have therefore examined several new techniques for dispersing asbestos and preparing composites in order to resolve the previously noted differences between our mixed MF/UAF (6 minutes Osterized) and Novabestos. Composites were prepared specifically to determine the influences of surfactant and of MF/UAF content on their strengths. The new dispersing techniques employed were: ultrasoneration, ball milling, roller milling, and mixing in a colloid mill. The two previous techniques, stirring and Osterizing, were also further employed.

1. Ultrasoneration

The Branson Sonifier was used in an attempt to produce UAF in an Aerosol OT dispersion of MF (commercial grade AY) by ultrasoneration. This device was extremely inefficient and the yield of UAF was quite low. No papers were made with the small amount of UAF product.

Monoisopropanolamine was also tried as the dispersing medium for asbestos in the Sonifier. A total of 4½ hours of ultrasoneration produced almost no UAF.

Figure 1. Photomicrograph of stirred asbestos dispersion in Aerosol OT solution.

Figure 2. Photomicrograph of 6 minute Osterized dipsersion of asbestos in Aerosol OT solution. Longest MF splint is 375 microns in length and 8 microns in diameter.

2. Roller Milling

A Type F 3-roll roller mill (2½" x 5") made by Charles Ross and Sons Company, Mixing and Grinding Machinery, was used to prepare dispersions of AY asbestos with (a) ethylene glycol, (b) Aerosol OT and (c) ammonium linoleate. A total of 40 passes for each composition was made through the mill with samples taken periodically for microscopic examination. It was hoped that varying ratios of MF/UAF would be obtained by this technique. However this did not prove to be the case. Microscopic examination showed that the roller milling produced relatively shorter and shorter MF on repeated passes through the mill and relatively little UAF was produced.

It was necessary to use 6% AY in the dispersions to have the viscosity required for handling in the roller mill. The thick, grease-like dispersions were diluted before making into paper. The ethylene glycol dispersion was diluted with ethylene glycol to the proper consistency for filtration (3% AY), filtered on sharkskin filter paper, pressed between blotters at 500 psi to a 50% wet pick-up and then dried at 80-90°C for several hours to evaporate off the glycol. The Aerosol OT and ammonium linoleate dispersions were carefully diluted with water to give 1½% AY dispersions and poured into Teflon wells to dry.

3. Homomixer

The Eppenbach homomixer, a high shear mixing device, was used to make dispersions of AY in ethylene glycol and in monoisopropanolamine, using mixing times of 1 minute and 30 minutes. Microscopic examination of the dispersions showed mostly MF after 1 minute mixing and a mixture of MF/UAF (largely MF), after 30 minutes of mixing. Papers were made by

filtration on sharksin and drying at 80-90°C.

4. Osterizing

This technique has been employed extensively in the course of this program to disperse MF to UAF. Some typical papers made with mixed MF/UAF and 100% UAF, obtained in Aerosol OT dispersion, are reported in Table 1. Dispersion of asbestos has also been carried out in organic liquids, typified by the following example:

A mixture of 3 parts AY asbestos and 97 parts ethylene glycol was dispersed by mixing for 6 minutes in the Osterizer. The resulting MF/UAF dispersion (which was similar in appearance to the aqueous dispersion shown in Figure 2) was filtered on sharkskin paper and the wet mat was dried at 80°C for 1 hour to evaporate the glycol, leaving a 100% asbestos paper.

5. Novak-Type Stirring

Using the Novak-prescribed technique of no-shear stirring of a dispersion consisting of 1 part AY asbestos, ½ part surfactant, and 98.5 parts water, we have produced UAF/MF dispersions. We have developed a technique for separating out the UAF and recovering a select fraction of the longest UAF. The technique has been used with Aerosol OT, sodium oleate, and morpholine linoleate surfactants. A typical procedure with Aerosol OT is:

The dispersion was stirred for a total of 5 hours and then filtered through a 3/32 inch thick sheet of 100 pore per inch, open cell polyurethane foam. This filter effectively removed the MF and the filtrate was a turbid dispersion of UAF. No visible particles could be seen in the filtrate when

examined by light microscopy. The UAF were then coagulated by the addition of ethanol to the filtrate to give long, fine fibrils which were recovered by spinning them onto a stirring rod. Shorter non-spinnable UAF were not recovered on the rod. The recovered long UAF were washed twice with ethanol and air dried. Carbon analysis of a typical sample showed that the fibrils contained a residual Aerosol OT add-on of 4.4%. The total yield of long UAF, based on the weight of AY asbestos in the original dispersion before stirring, was about 10%.

Two types of papers were made with these long UAF. The first type of paper was made by redispersing the fibrils in ethylene glycol with careful hand stirring, filtering the dispersion on sharkskin paper, pressing the wet mat at 500 psi to reduce the liquid content to 50%, and then drying at 85°C for 3 hours to evaporate off the glycol. The second type of paper was made by redispersing the long UAF in Aerosol OT solution (1 part UAF, ½ part Aerosol OT, 98.5 parts water) with hand stirring, pouring the entire dispersion into a flat, Teflon-coated pan, and evaporating to dryness at room temperature to form a paper containing 36 parts Aerosol OT per 64 parts UAF.

6. Ball-Milling

An AY asbestos-Aerosol OT mixture in water (½ part AY, ¼ part Aerosol OT, and 99¼ parts of water) was placed in a ball mill with flint pebbles and run for 16 hours. The resulting dispersion was filtered through a 100 pore/inch, open-cell urethane foam and the UAF was recovered by coagulation of the filtrate with ethanol as detailed above in A.5. The yield

of long, spinnable UAF was about 25% thus considerably better than the yield from the stirred dispersions.

Ball milling was also used to disperse asbestos in ethylene glycol. A mixture of ½ part AY asbestos and 99½ parts glycol was milled for 16 hours to produce a mixed MF/UAF dispersion. This was filtered through urethane foam to remove the visible MF and then the filtrate was coagulated by adding a large volume of water. No spinnable UAF was obtained. This may be due to an actual lack of extra-long fibers. It may also be due, however, to the fact that the fibers are in a glycol medium rather than a surfactant medium. This point has not yet been established. The UAF were collected by filtering on sharkskin paper and the wet mat formed was pressed, then dried at 85°C to remove the glycol and leave a paper of 100% UAF of uncertain fiber length.

Papers made with UAF or UAF/MF, obtained by these various techniques, were tested for strength both untreated and impregnated with resin. These papers thus afford the opportunity of assessing the relative effects of fibril diameter (MF vs. UAF), fibril length, and residual surfactant on the fibrils. Typical data are summarized in Tables 2 and 3.

Table 2 compares papers and composites made with fibrils obtained from ethylene glycol dispersions. Thus they are surfactant-free, except for the three made with spinnable UAF. Three contain 4.4 parts Aerosol OT per 95.6 parts UAF (as described above in A.5.). The surfactant content was verified by carbon analysis of the paper and indicates no further extraction of Aerosol OT by the glycol dispersing medium. All of these 100% asbestos papers, untreated, are shown to be weak. Among these the papers containing longer, dispersed fibrils (MF/UAF and long UAF) tend to be

TABLE 2. Effect of dispersing techniques on ethylene glycol paper and composites

Technique	Resin	Fiber Type	Paper Composition		Properties				
			Resin wt. %	Asbestos wt. %	Thickness mils	Density g/cc	% Void Space	Elongation %	Tensile Strength[2] psi
Ball Mill	None	UAF	0	100	10.6	0.53	79	3	120
	Phenolic	UAF	36	64	8.7	1.0	50	2	4400
Eppenbach	None	MF	0	100	12.7	.82	67	3	24
	Phenolic	MF	54	46	14.3	1.2	35	2	5400
	Polyester	MF	56	44	15.2	1.3	29	3	4100
	None	MF/UAF	0	100	14.3	.70	72	3	71
	Phenolic	MF/UAF	52	48	13.7	1.4	25	3	9500
	Polyester	MF/UAF	53	47	14.6	1.5	18	6	6800
Osterizer	None	MF/UAF	0	100	15.7	.65	74	6	120
	Phenolic	MF/UAF	54	46	12.5	1.5	18	5	10500
	Polyester	MF/UAF	55	45	15.4	1.4	23	6	3500
	None	UAF	0	100	17.2	.59	76	2	49
	Phenolic	UAF	53	47	16.0	1.2	35	3	6900
	Polyester	UAF	57	43	21.1	1.1	39	4	3900
No-Shear Stirrer	None	UAF[1)]	0	100	11.6	.94	62	2	90
	Phenolic	UAF[1)]	45	55	8.8	1.7	11	3	9300
	Polyester	UAF[1)]	36	67	9.2	1.6	14	4	6500

1) UAF fraction - contains 4.4% Aerosol OT.

2) Refer to page 10 for a discussion of how tensile strength is calculated.

TABLE 3. Effect of Dispersing Techniques on Aerosol OT Papers and Composites

Technique	Resin	Fiber Type	Paper Composition			Properties				
			Resin wt. %	Aerosol OT wt. %	Asbestos wt. %	Thickness mils	Density g/cc	% Void Space	Elongation %	Tensile Strength psi [3]
Osterizer	None	MF/UAF [1]	0	43	57	7.8	1.1	27	2	820
	Phenolic	MF/UAF [1]	53	15	32	9.9	1.5	5	3	4600
	Polyester	MF/UAF [1]	47	17	36	10.0	1.5	5	4	5700
	None	UAF [2]	0	37	63	7.1	1.2	25	1	610
	Phenolic	UAF [2]	53	15	32	8.5	1.4	12	2	2100
	Polyester	UAF [2]	47	17	36	10.4	1.4	12	4	2600
No-Shear Stirred	None	UAF	0	36	64	3.0	.83	49	5	980
	Phenolic	UAF	40	21	39	3.0	1.3	18	4	9500
	Polyester	UAF	41	21	38	4.3	1.0	36	3	4000
Roller Milled	None	MF	0	60	40	6.2	.93	29	7	220

1) Obtained by 6 minutes Osterizing.

2) Obtained by 90 minutes Osterizing.

3) Refer to page 10 for a discussion of how tensile strength is calculated.

stronger than the papers containing relatively shorter fibrils (90 minutes Osterized) or a major fraction of MF (1 minute colloid milling). Resin-impregnated, the tensile strengths show a similar dependence on fibril length and degree of dispersion. The strongest composites were those containing long UAF (from stirred dispersions), or UAF/MF (30 minutes colloid milling or 6 minutes Osterizing). The weakest composites were those containing MF splints (1 minute colloid milling) or relatively short UAF (90 minutes Osterizing).

Table 3 compares papers and composites made with fibrils recovered from Aerosol OT dispersions, and containing a residual deposit of the surfactant. The Aerosol OT/asbestos papers are considerably stronger than counterpart surfactant-free papers (Table 2). Among these we find improvement in strength with increased fibril length, just as in the surfactant-free papers. Aerosol OT appears to be an effective binder in this type of paper. Resin-impregnated, the tensile strengths of these surfactant-containing composites are about equal to the strengths of their no-surfactant counterparts. Again, the strongest composites were those reinforced with long UAF or MF/UAF and the weakest composites were those reinforced with MF (roller milled) or short UAF (90 minutes Osterizing).

Thus these data show that UAF reinforcement does not result in higher strength than UAF/MF reinforcement. The presence of as much as 20% surfactant (Aerosol OT) has no significant effect on the tensile properties of these asbestos/resin composites. As expected, tensile strength is increased by increasing UAF length. While these long, spinnable UAF are stronger than the shorter UAF obtained by 90 minutes Osterizing, they are not any better than the mixed MF/UAF (6 minutes Osterized).

B. Dispersing Media

In our earlier work on this program asbestos-resin composites were generally formed by impregnating prepared, dry papers with the matrix-forming materials and subjecting the composites to suitable curing conditions. Some composites were made without intermediate paper forming. In one such case we added polyvinyl alcohol solution to Aerosol OT dispersions of asbestos before evaporating to form papers. In a second case we added phenolic resin to ethylene glycol dispersions of asbestos (and to a mono-isopropanolamine dispersion of asbestos) before filtration. In each case the matrix was in intimate mixture with the asbestos in the dispersed state before the composite was formed. Typical composites made in this manner are compared, in Table 4, with their counterparts made in two steps (paper formation followed by impregnation). The composites made directly from the resin/asbestos dispersions show somewhat higher strengths than the composites made by resin impregnation of preformed papers. This suggests that we may have obtained improved resin-asbestos bonding in the former. The difference in the two phenolic specimens is slight, but in view of the equal densities is probably real. In the PVA specimens the difference is more significant, particularly since the weaker specimen has the higher density.

More recently we have investigated the possibility of using a resin precursor itself as the dispersing medium thus obviating the problems associated with the removal of solvent from asbestos/resin solution systems of the types shown in Table 4. Two liquid resin precursors have been found to be effective in dispersing MF to UAF and have been extensively explored. These are linoleic acid and a methyl hydrogen siloxane (DC 1107). The

TABLE 4. Comparison of Resin/Asbestos Composites made with and Without Intermediate Paper Formation

PVA Binder

Composite Made From:	Composition of Composite			Physical Properties			
	Asbestos %	Aerosol OT %	PVA %	Thickness mils	Density g/cc	Elongation %	Strength[1] psi
Resin impregnation of paper	36	21	43	4.1	1.2	3	3800
Direct asbestos/resin mixture in water	39	22	39	5.9	0.86	4	7700

Phenolic Binder

	% Asbestos	% Phenolic Resin				
Resin impregnated paper	64	36	8.7	1.0	2	4400
Direct asbestos/resin mixture in ethylene glycol	70	30	6.7	1.0	2	5200

[1] Refer to page 10 for a discussion of how tensile strength is calculated.

preparation of composites from these media was done as follows:

1. Composites from Linoleic Acid Dispersions

AY asbestos (3 parts) was dispersed directly in linoleic acid (97 parts) for 6 minutes in the Osterizer. Papers were formed by filtration on sharkskin. The filtered paper was pressed between blotters to reduce the liquid to 50% wet pick-up. Part of the paper was cured by heating in air at 160°C for 24 hours to effect polymerization. A still wet part of the paper was suspended in styrene vapor for 24 hours in a vacuum before curing at 160°C for 24 hours. As shown in Table 5, the asbestos-reinforced papers had good strengths despite the moderately low densities which indicate about 43% void volume. If any copolymerization of linoleic acid and styrene occurred it did not result in any higher strength in this composite compared to the one not exposed to styrene.

2. Composites from DC 1107 Silicone

AY asbestos (3 parts) was dispersed in silicone DC 1107 (97 parts) in the Osterizer for 6 minutes. Papers were formed by filtering the dispersion on sharkskin, pressing the filtered paper between blotters at 500 psi to a 50% wet pick-up and then heating for 24 hours at 160°C in an attempt to cure the silicone. We were not able to effect a cure of the silicone, even when the heating was continued for several days. It has been found that this silicone will cure when the paper has been precoated with surfactants (Aerosol OT and sodium oleate) but will not cure fully on pure asbestos (ethylene glycol papers). This point is discussed in detail in section C, below, where the strength of the not completely cured paper is reported.

TABLE 5. Composites from Linoleic Acid/Asbestos Dispersions

Composite Composition			Physical Properties			
Asbestos %	Linoleic Acid %	Styrene %	Thickness mils	Density g/cc	Elongation %	Tensile Strength[1] psi
70	30	0	14.6	0.98	4	4500
39	39*	22*	15.6	0.85	4	4600

* These data are based on the pick-up of styrene by the wet, linoleic acid/asbestos mat. Oven heating may have driven off some portion of unreacted sytrene.

[1] Refer to page 10 for a discussion of how tensile strength is calculated.

3. Composites from Linoleate Soaps

Another approach to obtaining good matrix/asbestos bonding has also been investigated. In this approach we have used water-soluble, monomeric resin-precursors which, themselves, serve the added function of the dispersing surfactant in aqueous systems for dispersing MF to UAF. Compounds which we have found to fill this dual role are the basic soaps of linoleic acid, in which the base is volatile. This approach appeared particularly interesting in view of the following observations we have made during the course of this program:

(1) When asbestos is dispersed in aqueous surfactant solutions, the fibrils become coated with a deposit of surfactant, tightly adherent to the fibrils. This is evidenced, for example, by the Aerosol OT surfactant systems, such as described above in A.5.

(2) In general it has been noted that more dense, stronger papers are obtained from a slow evaporation of aqueous surfactant dispersions than from filtered aqueous dispersions or from either evaporated or filtered organic media dispersions.

(3) Linoleic acid appears to be a good matrix for asbestos reinforcement, as evidenced by the data in Table 5.

Both the ammonium and morpholine soaps of linoleic acid have been used.

a. Ammonium Linoleate

A soap solution was prepared which had 5% linoleic acid and sufficient excess ammonium hydroxide to maintain a pH of 9-10. This was used as stock to prepare dispersions of AY asbestos. A number of compositions were investigated. A workable composition was found to contain 2 parts AY to 1 part of linoleic acid in 97 parts of water with ammonium hydroxide to pH 9. It was Osterized 6 minutes, poured into a Teflon well,

evaporated to dryness (driving off water and ammonia), then press cured at 500 psi and 100°C for 1 hour to produce a composite reinforced with MF/UAF.

Another dispersion containing 6.2 parts of AY to 1.6 parts of linoleic acid with ammonium hydroxide to maintain pH 9 and 92.2 parts of water was roller milled for 40 passes. The resultant mix was diluted with dilute ammonium hydroxide to pouring consistency (about 2% AY), poured in a Teflon well, evaporated to dryness and press cured at 500 psi 1 hour at 160°C to produce a composite reinforced with short MF and containing little UAF

The volatilization of ammonia was very rapid from these papers and tended to promote segregation of linoleic acid and asbestos in the composites. Apparently the asbestos tended to floc out (as the ammonia volatilized faster than the water) and settle to the bottom of the well.

b. Morpholine Linoleate

In order to control the rapid loss of alkalinity a less volatile base, morpholine, was used. This base did give better paper, in terms of appearance, than did the ammonium soap. Examination of a range of compositions showed that satisfactory dispersions could be made using 6.2 parts of AY to 1.6 part of linoleic acid adjusted to pH 9 with morpholine in 92.2 parts of water. The dispersions were Osterized for 6 minutes, poured into a Teflon well, evaporated at room temperature to dryness and the paper then cured overnight at 120°C.

In addition to these three types of papers made with mixed MF/UAF obtained from linoleate soap dispersions, papers were also made with all long fiber UAF.

To obtain long fiber UAF, ½ part of AY was dispersed in 99¼ parts water containing ¼ part linoleic acid with sufficient excess morpholine to give pH 9 by stirring with a Hiller stirrer for 5 hours. The resulting dispersion

was filtered through 100 pore/inch polyurethane foam to remove MF. The UAF was coagulated by diluting the filtrate with 20 volumes of water. The long UAF was spun out on a stirring rod, washed twice with ethanol and air dried. Part of the long UAF was redispersed in linoleic acid by careful hand stirring and paper was made by filtration on sharkskin. The filtered paper was pressed at 500 psi between blotters to give a 50% wet pick-up and was then oven cured at 100°C for 48 hours.

Another portion of the long UAF was redispersed in a 1% morpholine linoleate solution by careful hand stirring (2 parts UAF to 1 part of linoleic acid, adjusted to pH 9 with morpholine). The dispersion was poured into a Teflon well and air dried for 72 hours. The paper was then oven cured for 48 hours at 100°C. Physical properties of the asbestos-reinforced composites made from these various linoleate dispersions are summarized in Table 6. Included for comparison is data for a composite prepared from a direct dispersion of asbestos in linoleic acid. Although the composites made from linoleate soap dispersions are all strong, they are not as strong as the one made from a direct linoleic acid/asbestos dispersion, suggesting that we may have some residual soap. However, at present this effect is unexplained. Further, there is a differences between the ammonium and morpholine linoleate composites, the morpholine soap producing a somewhat weaker composite. This suggests that we may not have completely gotten rid of the morpholine. As expected, the weakest composite of the group is the one reinforced by the MF/UAF mixed fibers obtained by roller milling. These fibers are mostly short MF, the proportion of UAF being very low, as contrasted with the low MF/high UAF ratio in 6 minute Osterized dispersions.

TABLE 6. Composites from Linoleate Soap Dispersions of Asbestos

Soap Base	Dispersing Technique	Type of Reinforcement	Wt. ratio of asbestos/linoleic acid in composite	Physical Properties of Composite			
				Paper Thickness mils	Density g/cc	Elongation %	Tensile Strength[3] psi
Ammonia	Osterizer	MF/UAF	67/33	3.0	.74	5	2700
Ammonia	Roller mill	mostly MF	79/21	5.5	.88	6	870
Morpholine	Osterizer	MF/UAF	79/21	5.2	.73	5	1200
Morpholine	No-shear stirrer	long UAF	67/33	3.5	.96	4	2200
None[1)]	No-shear stirrer	long UAF	67/33	12.6	1.0	6	2100
None[2)]	Osterizer	MF/UAF	70/30	14.6	.98	4	4500

1) Long UAF was recovered from a stirred morpholine linoleate dispersion, then redispersed in linoleic acid.

2) Direct dispersion of asbestos in linoleic acid.

3) Refer to page 10 for a discussion of how tensile strength is calculated.

The long UAF is about equal to MF/UAF (obtained by Osterizing) in these composites, just as it was equal to MF/UAF in the composites reported in Tables 2 and 3.

C. Coupling Agents or Surface Conditioners

As described in section B.2, DC 1107 does not cure on pure asbestos. Whether the silicone is used as a dispersing medium or is added to a dry preformed paper made from an ethylene glycol dispersion of asbestos, the silicone will not cure. On the other hand silicone applied to Novabestos paper (which contains sodium oleate) does cure satisfactorily as shown in Table 7.

Therefore, to test whether specific conditioners for effecting cure exist, some pure asbestos in the form of dried glycol papers was treated with (1) Aerosol OT, (2) γ-aminopropyltrimethyoxy silane and (3) sodium oleate by soaking in solutions of these and subsequently evaporating the solvent from the soaked paper. The treated papers (containing 5 to 25% conditioner) were air dried, then treated with DC 1107 silicone by dropwise impregnation, and heated for 24 hours at 160°C in an attempt to effect curing. Physical properties of these composites are reported in Table 7. Data for the sodium oleate "conditioned" paper are not given because an accurate thickness measurement could not be made due to its high void volume and rough texture. DC 1107 did cure on this paper and we roughly estimate that its strength should be equal to that of the Aerosol OT - conditioned paper. The data in Table 7 show that only partial curing of DC 1107 occurs on pure asbestos. The presence of sodium oleate or Aerosol OT allows more complete curing of this silicone, while gamma aminopropyltrimethoxy silane (a commonly used

TABLE 7. Effect of Surface Conditioners on Effectiveness of Silicone Treatment

Base Paper	Conditioner Added	Paper Composition			Properties			
		Conditioner wt. %	Asbestos wt. %	DC 1107 wt. %	Thickness mils	Density g/cc	Elongation %	Tensile Strength[2] psi
Glycol	None	0	100	0	14.4	0.67	8	90
	None	0	54	46	15.9	1.1	1	460
	Aerosol OT	25	75	0	12.8	.89	—	160
	Aerosol OT	17	35	48	21.1	1.1	5	3200
	γ aminopropyl-trimethoxy silane	5	95	0	14.3	.65	2	100
		2.5	51.5	46	15.5	1.2	1	330
Novabestos	None	5.5	94.5[1)]	0	3.4	.57	7	520
	None	3.7	60.3[1)]	36	4.7	.79	3	4500

1) Novasbestos used as received, containing 5.5% oleate soap.

2) Refer to page 10 for a discussion of how tensile strength is calculated.

coupling agent in glass fiber-reinforced composites) inhibits curing.

IV. CONCLUSIONS AND RECOMMENDATIONS

The feasibility of reinforcing polymeric structures with UAF has been demonstrated. The strength properties of UAF-reinforced composites have been found to be influenced by the following variables: length of the reinforcing fibrils, presence of conditioner or coupling agent on the fibrils and nature of the polymer matrix. These effects are certainly not surprising since they are well-known in the field of reinforcement with macroscopic-sized filaments and whiskers. Our UAF-reinforced composites, like the conventional composites reinforced with macroscopic fibers, display the expected improvements in properties on elimination of voids and on densification of the structures. What is surprising in the extra-long UAF-reinforced composites is that their strengths are not significantly higher than those of composites reinforced with MF/UAF mixtures. It is to be expected that the extra-long UAF, being the most flawless form of asbestos, should be considerably stronger on a psi basis than the MF asbestos bundles. A reasonable estimate for the ultimate tensile strength of UAF is at least one million psi, considering that tensile strengths as high as 800,000 psi have actually been measured for small diameter MF. Thus our composites reinforced with about 20 v/o UAF which have strengths of about 10,000 psi fall far short of their potential, utilizing less than 5% of the fibril strength. The fact that our isotropic UAF-reinforced composites are somewhat weaker than the composites reinforced by the commercial, oriented asbestos paper is almost certainly due to the orientation. Indeed, if unidirectional orientation of UAF can be achieved, a considerably stronger

composite should result. In the technology of whisker reinforcement with sapphire and metallic whiskers it has been demonstrated that 50% utilization of fiber strength can be realized. It should be possible to utilize 50% of the asbestos fibril strength by selection of the proper matrix material and by orientation of the fibrils in the matrix. Thus with 20 v/o UAF reinforcement it should be possible to obtain composites having tensile strengths greater than 100,000 psi.

In regard to fibril conditioning and fibril-matrix bonding we have found that the types of systems conventionally used with MF asbestos are also satisfactory for UAF. Of potential interest for UAF reinforcement is the opportunity (for the first time in asbestos reinforcement) of obtaining complete UAF-matrix bonding on a molecular scale. We have demonstrated this in our experimental systems based on linoleic acid (free acid or soap), in which the UAF dispersion is carried out with the monomeric form of the final polymeric matrix.

We recommend that further work on UAF-reinforced polymeric structures, particularly from the standpoint of attaining the highest possible strength be conducted in the following areas:

1. Fibril orientation. Since the UAF are uniquely small in diameter, attempts should be made not only to take advantage of the readily obtainable high aspect ratios in isotropic structures but also to orient the UAF for anisotropic structures. As noted above, fibril orientation in a composite can result in a several-fold improvement in strength over the comparable iostropic composite. This important point should be thoroughly exploited in future work.

2. Conditioners and coupling agents. Although they are commonly used in glass fiber-reinforced composites, coupling agents and conditioners are not purposefully employed in MF asbestos-reinforced composites. Their utility in UAF-reinforced composites should be explored well beyond our preliminary tests. It is noteworthy that Novabestos, conditioned with sodium oleate, gives very strong composites with phenolic resin despite the fact it contains mostly MF splints, has only 10 to 15% UAF, and in its strong (oriented) direction is only one-half to one-third as strong as our unoriented papers made from high-UAF content (80% UAF) Aerosol OT dispersions. We can tentatively and logically ascribe the reinforcing ability of Novabestos to the oleate conditioner on the surface of the fibers. Oleate-conditioned fibrils should be one of the first areas to be explored in future work. It appears likely that conditioners (and coupling agents) could play an important role in UAF-reinforced composites because of the very high fibril surface area/volume ratio of UAF compared to macroscopic fibers.

3. Monomers having specific adhesion for UAF. It appears that excellent matrix-UAF adhesion can be promoted by effecting the dispersion of MF to UAF directly in a matrix precursor. Monomers should be selected or tailor-made which exhibit both good dispersing ability (and correspondingly strong specific adhesion for UAF) and the ability to form suitable matrixes either by homopolymerization or copolymerization with an auxiliary resin precursor.