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UNION CARBIDE OLEFINS COMPANY

Research and Development Department
South Charleston 3, West Virginia

MONTHLY REPORT

Subject: Process Development - Program III
Hydrocarbon Resins
Investigation of Hydrocarbon Resins as Binding Agents for Coalinga Asbestos

Date: May 31, 1963

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Summary

On the basis of preliminary experimental work, resins produced from Unsaturate Oil show considerable promise as binding agents for Coalinga asbestos. Applications include uses in such building materials as wall board, floor tile, conduit and general service pipe. For materials employing 2-to-1 mixtures of asbestos to binder, flexural strengths above 2500 psi were found with each of the three binders evaluated. The specimens using Prepolymer U-311 or a soft hydrocarbon resin prepared from C Cut of Unsaturate Oil as binder required heat-curing. Curing by baking in air proved to be more effective than by baking in a nitrogen atmosphere; a temperature of 200°C was better than either 250° or 150°C; and strength and rigidity increased with time of baking in air in limited studies for periods of 2 to 64 hours. The third binder, a hard resin (softening point, ~95°C) prepared from D Cut of Unsaturate Oil and fused with the asbestos in a press, yielded without any cure a material which had a flexural strength of 2530 psi, which was higher than the average for the other two binders, and was less rigid.

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Introduction

The Union Carbide Nuclear Company owns a large California deposit of Coalinga asbestos, a short-fiber asbestos of superior quality occurring in such a way as to make possible very high yields and purity. This deposit is large enough to supply the world for 200 years and is advantageously located for much

of the U. S. market in competition with Quebec asbestos, currently the leading source. After two years of market studies and development work, a small asbestos plant is under construction.

One of the most advanced new applications of this asbestos is the thermosetting material designated F-100. This is a 4:1 blend of Coalinga asbestos and a Union Carbide Plastics Company phenolic resin which is applied in the form of an aqueous solution. The F-100 has been successfully extruded and cured in the form of pipe and panels in pilot plant quantities and is expected to compete favorably in the building industry because for many applications it has superior properties at a lower cost.

The evaluation of other resins as binders for asbestos of course continues, and thus hydrocarbon resins from Unsaturate Oil were considered. Some of the advantages of the hydrocarbon resins seem to be a resin cost of only about half that of the phenolic resin, avoidance of the several-day water-removal step required with the phenolic resin, and lighter-colored products.

Preparation of Asbestos-Resin Blends

At least two methods of blending hydrocarbon resins with asbestos are possible: a hard thermoplastic resin can be blended under heat and pressure, or a soft resin can be blended with asbestos under pressure alone and then later further thermopolymerized to a hard resin. So that our work would be consistent with the room-temperature blending and extrusion done in the Nuclear Company's pilot plant, the latter method was used first.

Two soft resins were tested, Prepolymer U-311 and a light-colored hydrocarbon resin prepared from C Cut of Unsaturate Oil (Notebook reference: 1947-82-14). With each resin equal parts of standard-grade Coalinga asbestos and the resin were hand-kneaded for about twenty minutes until a putty-like composition resulted. Excess resin could be squeezed out under high pressure; so an additional part of Coalinga asbestos was worked into each blend on a 3-by-8-inch rolling mill (by Mr. R. L. Kirk of the Chemicals Company). The blend banded tightly to the roll at first but began to separate rather readily by the end of the ten-minute milling operation. The 2-to-1 mixture of asbestos and resin appeared to have reached a maximum desirable proportion of asbestos, because when more was added the blend became too dry and stiff for satisfactory working.

Most of the blends have been stored in capped bottles to prevent loss of volatile components, and a nitrogen atmosphere has been used to minimize air oxidization. Samples left open to the air slowly hardened at the surface. While Coalinga asbestos by itself is light gray in color, it darkens considerably on being wetted by an organic material; and the blend containing the light-colored hydrocarbon resin is very little lighter in color than the blend with the very dark Prepolymer U-311.

Initially the Prepolymer U-311 was pressed at about 3000 psi in a mold which gave a thickness of 1/16 inch. As thicker samples were recommended for flexural strength and modulus measurements, a mold was then obtained to give a thickness of 1/8 inch. The thinner samples, however, served to show the effect of thickness on cure time. Test strips 1/4 inch wide and about 4 inches long were then punched with a die from the pressed material.

Because no Banbury mixer was available to blend small quantities of hard resin with asbestos under heat and high shear, the hard hydrocarbon resin which had been prepared from D Cut of Unsaturate Oil (Notebook reference: 1894-89-06) was ground in a mortar and screened through a 60-mesh sieve. One part of the powdered resin and two parts of Coalinga asbestos were mixed by rolling in a jar for 25 minutes. A press heated to 120-130°C was used to repeatedly fuse and compact the mixture until a "pancake" of 1/8-inch thickness was formed. Total time under heat and pressure was 25 - 30 minutes. While the "pancake" remained thermoplastic, it was too tough at room temperature to punch out strips. A slightly crude test strip, however, was cut out with a knife and this specimen was not cured; its flexural strength and modulus (rigidity) were then measured.

In future experiments it is planned to prepare test specimens by extrusion. Strength and uniformity are improved in material which has been extruded over that which has been compressed, representatives of the Nuclear Company at Sterling Forest have stated. An extrusion cylinder with an inside diameter of two inches and equipped with a removable heating jacket has now been made for extruding strips with a cross section of 1/8 inch by 1/4 inch.

Method of Curing

The material prepared from the two soft resins required curing by heat-polymerization, which was done in a small laboratory

furnace. A two- or three-stage curing with successively higher temperatures was employed in most cases, the purpose being to allow polymerization of the more volatile components before the final curing temperature was reached. The range used was 150 to 250°C, and curing time was from 2 to 64 hours. Most specimens were air-cured, but in a few of the earlier experiments, curing was done in a nitrogen atmosphere in an unsuccessful attempt to preserve the starting resin's thermoplastic nature or at least to reduce stiffness appreciably in the final material. Because the first strips curled somewhat during the baking, later specimens were cured between ~3/32-inch-thick stainless steel plates.

Physical Property Measurements

In this early work aimed at a possible asbestos-hydrocarbon resin material, the physical properties chosen as most significant to test were flexural strength and flexural modulus (in practice often used interchangeably with modulus of elasticity). Flexural strength is defined as the resistance to breaking of a strip as it is bent across its main axis. It is calculated according to the formula

$$S = \frac{3}{2}\frac{P_2 l}{bh^2}$$

where S = flexural strength, as psi
P_2 = force at break, pounds
l = length of span, inches
b = width of strip, inches
h = depth of strip, inches

The flexural modulus, expressed as E (psi), which is a measure of the stiffness or rigidity of a material, is defined as the load per unit area required to give unit deformation. It is calculated from

$$E = \frac{P_1 l^3}{4\delta bh^3}$$

where P_1 = force at linear portion of stress/strain curve, pounds
δ = deflection at load P_1, inches
(l, b, and h same as above)

These physical properties are being measured by us on a Model TTC Instron Testing Instrument belonging to the Chemicals Company Research and Development Department, through the courtesy of Mr. Keith L. Smith and his group.

Discussion of Results

Because several areas of unfamiliarity were involved at the start, this work in its early stages is a scouting type of investigation. Many of the methods used and the selection of variables investigated are preliminary in nature, and some of the interpretation of data is as yet inconclusive. However, it is felt that considerable knowledge and experience has been gained thus far, many conclusions are quite clear, and fairly good definition has been achieved as to the direction of the work and variables to be studied at this point.

The first series of specimens tested, whose composition was 2:1 asbestos : Prepolymer U-311 (Table I, Samples 1930-86-2 through -10), proved to have good flexural strength (1780 to 4120 psi). While they were brittle, their flexural modulus values were acceptable (900,000 to 1,330,000 psi). Since these samples had been heat-cured in air and since oxidation of reactive constituents would be expected to have an effect on the structure and characteristics of the polymer formed, several specimens were cured in a nitrogen atmosphere at conditions otherwise identical to those for air-cured specimens. As can be seen from the following table, the flexural modulus was not appreciably lowered, but the material generally had noticeably less flexural strength.

EFFECT OF CURING ATMOSPHERE

Type of Material	Final Curing	Flexural Strength (psi)		Flexural Modulus (psi x 10^3)	
		N_2	Air	N_2	Air
U-311 (1/16")	6 hours at 250°C	2170	2490	990	1090
U-311 (1/8")	10 hours at 250°C	2080	2140	540	560
C Cut resin (1/8")	10 hours at 250°C	1660	2440	600	740

Therefore it seems reasonable to conclude that oxidation during curing actually imparts strength and rigidity to the material. Of course, it is also possible that those specimens cured under a slow nitrogen purge and without being between two metal plates experienced a greater loss of volatile components, and accordingly a weaker polymer resulted.

A primary consideration is the effect of curing time and temperature on the properties of the material produced. It is apparent from limited results to date, summarized on the following page, that strength increases with curing time in air up to some point beyond 10 hours.

EFFECT OF CURING TIME AND TEMPERATURE

Type of Material	Final Curing	Final Curing Time (hours) (Flexural strength (psi)					
		2	4	6	8	10	64
U-311 (1/16")	250°C in air	1780	2290	2490	3160	4120	
" (1/8")	" " "					2140	
" (1/8")	200°C " "					2630	2210*
" (1/8")	150°C " "		1200	1090		1540	
C Cut resin (1/8")	250°C in air					2440	
" " (1/8")	200°C " "					2870	3490
U-311 (1/8")	250°C in N_2		2300			2080	
C Cut resin (1/8")	" " "		2090			1660	

*Value appears low; specimens were layered, probably as a result of poor forming.

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A temperature of 150°C seems too low, and 200° appears to be better than 250° for a ten-hour cure; however, more study is also needed here.

One very conspicuous fact is seen in a review of the above table (greater detail in Table I): the 1/16" strips prepared from U-311 Prepolymer were much stronger than the 1/8" strips. (They were also not as dark a brown in color.) As far as is known, the 1/16" set differed from the other set in only three respects: they were pressed at about three times the pressure; they were thinner; they were not cured between stainless steel plates. On the basis of the Sterling Forest experience, the higher pressure could have a detrimental effect (unless it forced better wetting of asbestos by hydrocarbon following probable inadequate blending). The other two differences would certainly have facilitated more complete oxidation of the material; and the results again indicate that oxidation increases strength and rigidity, as stated earlier.

From the data for the specimens cured for 4 and 10 hours in a nitrogen atmosphere, it appears that the material weakened a little during the longer baking period. No logical explanation is offered for this occurrence, unless it could have resulted from a faulty test sample. Presently no further study along this line is planned because, as discussed earlier, air-curing has consistently produced stronger material than nitrogen-curing.

Mr. Hal Reichard and Mr. Norman Setter of the Nuclear Company have stated that these early results for all three Unsaturate Oil-derived mixtures are rather promising. They predict noticeable improvement when extruded material is tested, particularly if more vigorous mixing is accomplished first. A flexural strength above 1000 psi is considered satisfactory for a number of applications, as are flexural modulus values up to somewhat over 1,000,000 psi in combination with high strength. For some applications a modulus in the 200,000-to-600,000 range is preferred. The following table summarizes by material type the more significant results obtained.

COMPARISON OF RESINS

Method of Specimen Preparation	Flexural Strength (psi)			Flexural Modulus (psi x 10^3)		
	D Cut Resin	U-311	C Cut Resin	D Cut Resin	U-311	C Cut Resin
Dry-mixed, fused and compacted, not cured	2550			420		
Cured in air, 250°C, 10 hrs		2140	2440		560	740
" " " 200°C, 10 hrs		2630	2870		640	790
" " " 200°C, 64 hrs		2210*	3490		560	640
Cured in N_2, 250°C, 4 hrs		2300	2090		540	640
" " " " 10 hrs		2080	1660		540	600

*Value appears low; specimens were layered, probably as a result of poor forming.

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Early in this work it was noted that the dark brown hydrocarbon-asbestos material lightened appreciably and almost instantly upon contact with even a slight amount of water. Some experiments were then run (See Table I) involving various degrees of wetting of uncured material both before and after milling. This was in the hope of obtaining a lighter-colored cured material without appreciable loss of strength. However, the results obtained indicate that this is not feasible under the conditions tried. Even though the flexural strength of some wetted samples was not greatly lowered, the material swelled to some extent and separated in spots and generally appeared unsatisfactory. In the case of a slightly dampened test strip (1961-22-3), the final color was only a little lighter, and the surface appeared blistered or wrinkled.

In one of the later experiments (1961-40), the loss in weight during baking was measured, with the following figures

obtained:

Weight Loss of 2:1 Asbestos: U-311 Prepolymer During Baking at 150 C

After 4 hours:	After 6 hours:	After 10 hours:
3.93%	3.39%	3.91%

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Program

Of the many areas of investigation suggested by the work so far, it is planned to give attention next to:

1. Extrusion of blends of both hard and soft resins with Coalinga asbestos.
   a. Proper conditions (temperature, pressure) for effective extrusion.
   b. Effect of single- versus multiple-extrusion.
2. Continuation of experiments on curing of soft resins.
3. Continuation of strength and rigidity tests.
4. Some attention to other properties, such as hardness (indentation), impact resistance, and compressive strength.
5. Effect of drying of asbestos to achieve better wetting by hydrocarbon.
6. Limited studies of resins by themselves. Extrusion, curing, physical property tests.

CWS:iew

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Attachment: Table I

cc: Mr. H. T. Reichard, UCNC
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TABLE I

HYDROCARBON RESINS AS BINDING AGENTS IN 1:2 BLENDS WITH COALINGA ASBESTOS

Conditions of Preparation and Physical Property Tests of Product

Material	Sample No.	Curing Conditions[a] Pressed at PSI	Hours at 150°C	Hrs. at 200°C	Hrs. at 250°C	Atmosphere	Sample Thickness	Physical Properties[b] Flexural Strength, PSI	Flexural Modulus, PSI	Remarks
2:1 Asbestos: U-311	1930-86-2	Up to 3000	4	2		Air	1/16"	1780	900,000	1930-86 series specimens were
	-4		4	4				2290	990,000	prepared by E. G. Caplisch.
	-6		4	6				2490	1,090,000	Ref: Mem. 855-2307-6230, 4/22/63.
	-8		4	8				3160	1,160,000	
	-10		4	10				4120	1,330,000	
	-N6		4	6		N_2		2170	990,000	
2:1 Asbestos: CCur Resin	1961-20-1	700-1000	2	4		N_2	1/8"	2090	640,000	
	-2		2	10		N_2		1660	600,000	
	-22-1		2	10		Air		2440	740,000	
	-38		4	10				2870	790,000	
	-45-64		64					3490	640,000	
	1961-21-1		2	4		N_2		2300	740,000	
	-2		2	10		N_2		2080	740,000	
	-22-2		2	10		Air		1980	650,000	
	-3		2	10				1330	380,000	Slightly dampened before baking
2:1 Asbestos: U-311	-23		1/2	10				890	156,000	Dampened before pressing
	-24-1		10	—				2630	640,000	
	-2		10	—				2290	390,000	Immersed in H_2O 10 sec. before baking
	-3		10	—				1600	260,000	" " " 30 sec " "
	-37A		2	10				1830[c]	490,000	
	-37B		2	10				2300	580,000	Stored under N_2 3 wks. before baking
2:1 Asbestos:	-40-4		4	—				1200	170,000	
	-40-6		6	—				1090	140,000	
	-40-10		10	—				1540	300,000	
	-44-64		64	—				2210[c]	560,000	
2:1 Asbestos: B Cur Resin	1961-25	700-1000	—	—		—		2550	420,000	

Notes:

1. 1961-25 was ground to 60 mesh, dry-mixed, then used and compacted at ~120°C in 5 stops totalling 25-30 minutes.
2. For all liquid resin samples, equal parts were hand-kneaded, then 2nd part asbestos blended in by 10-min. milling.

a Heat-cured specimens placed between two 3/32" S.S. plates during baking except (1) those cured in N_2 and (2) the 1/16" strips (1930-86 series).

b Measurements made on Model TTC Instron Testing Instrument. Rate of deflection was 0.1"/minute. Figures given are averages of 3-6 tests — more than 3 when necessary to obtain reasonable agreement.

c Values probably are low; specimens were layered, probably as a result of poor forming.

C. W. Schersten 5-31-63

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