F. H. Larison

TECHNICAL SERVICE REPORT

by

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The Use of Calidria SG-210 Asbestos in Dry or Ready-Mix Tape Joint Compounds

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Chemicals and Plastics
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What Asbestos Fibers Do in Tape Joint Compound

Asbestos performs a number of functions in commercial ready and dry-mix tape joint compounds. The primary function is to form the backbone or "web" for the inert fillers and film formers to associate with. Upon drying, or film cure, the asbestos adds a significant amount of dimensional strength to the applied materials. The influence of asbestos on other formulated performance properties depends upon the particle size and concentration level with respect to the other inert fillers.

Asbestos functions as a secondary bodying and thickening agent, in wet formulations, via the water absorption capacity of the fiber. In this capacity, it contributes to the reduction of product density in relationship to the concentration level employed in the formulation. This comes about as a result of the increased water demand. The water absorption efficiency is a function of the particle size and other physical properties of the asbestos.

Finally, perhaps more than any other filler, asbestos contributes significantly to the formulated compound smoothness, cratering, and "wet edge" properties. This is because of the fibrous nature of asbestos particles. In like manner, both the asbestos particle size and concentration level will determine, to a large extent, the smoothness of the feathered edges.

On the negative side, of the variety of inert fillers employed in a joint compound, asbestos and clays contribute most to the nailhole cracking problems. In the process of water absorption, asbestos particles swell. On drying, these particles shrink with the release of water. Although the swelling is necessary for good product body, asbestos at too high a level can be the single largest contributor to thick layer joint compound shrinkage cracks. Product particle size uniformity is therefore of utmost importance in regard to reproducible built-in properties of a formulated tape joint compound.

Special Properties of "Calidria" Asbestos

Most asbestos materials, marketed commercially for use in tape joint compounds, contain rock dust and other abrasive type fillers, that have no specific desirable effects on joint compound performance. "Calidria" SG-210 and SG-130 asbestos are produced by a proprietary manufacturing process that yields essentially a pure asbestos fiber content. The SG-210 product is preferred for ready-mix smoothness and water absorption efficiency. Another feature is the unique shape and physical structure of the "Calidria" asbestos fibers. The micro-size particles are actually "fibrils" and the respective stems are hollow; hence, the fibers have a tremendous water absorption capacity. In like manner, there are more "active sites" for other inert fillers to associate with, in formulated film formation. As a result, "Calidria" asbestos generally goes twice as far, on a pound for pound basis, as the Canadian and other commercial types used in tape joint compounds. It is these physical properties that enhance the wet joint compound workability and performance properties mentioned above.

How to Use "Calidria" Asbestos in Tape Joint Compounds

"Calidria" asbestos can be used in dry or ready-mix compounds, with very little change in formulation parameters. Since "Calidria" SG-210 will go twice as far as similar Canadian types, a good substitution starting point is

one-half as much. The formulation weight difference is best made up with mica or calcium carbonate dry filler.

The typical product characteristics of "Calidria" SG-210 and SG-130 are listed in Table I. The SG-130 is shown, because it can be used in formulations where surface smoothness is not as desirable as that obtained with SG-210 asbestos.

The relationship of "Calidria" asbestos fiber physical properties to subsequent oil or water demand characteristics are depicted in Figure 1. In Figure 1, these absorption characteristics are compared to typical commercial grades regularly employed in joint compounds. The data, in Figure 1, show that a good "Calidria" asbestos substitution starting point is at about 50 percent, by weight, less than other typical commercial asbestos, without changing significantly the original formulation water demand (i.e. one-half the amount of other sources). The weight differences can be made up with either additional amounts of calcium carbonate or mica fillers. The latter is preferred with respect to ready-mix water demand and good nailhole cracking resistance. No other changes are necessary in the formulation.

Three suggested tape joint compound ready-mix formulations are listed here to depict the use of Calidria SG-210 asbestos. These are listed in Tables II, III, and IV. These formulations differ in both the ratio and types of additives, to introduce desired formulation end-use properties. For example, the suggested bedding coat material, Table II, does not have as smooth a dry surface, but should fill the primary requirements of good tape adhesion and a minimum amount of thick layer cracking. The general purpose formulation, Table III, should depict good overall working properties and have better wet edge and surface smoothness than the bedding coat material. A topping coat product, Table IV, should exhibit a minimum amount of volume shrinkage,(note the higher density), have exceptional surface smoothness, and wet edge. In addition, a minimum amount of sanding is desirable for topcoat materials. In actual practice, the bedding and top-coat materials are giving away to the general purpose types.

If Canadian or other types of asbestos were used in these suggested formulations, it would be at double the concentration level indicated to achieve essentially the same water demand. In like manner, the higher asbestos level dry compound surface smoothness would not be as evident with everything else being equal.

The formulations listed here are merely suggested ones. Experienced tape joint compound formulators have their own source of fillers and usually employ other ingredients to fit particular geographic conditions and subsequent end-use requirements. In the case of asbestos, the choice is generally between the Canadian and "Calidria" types. It is a matter of grades employed, efficiency, and effect on compound workability and dry-film cratering. In these important areas, "Calidria" SG-210 asbestos shows extremely good properties in either dry or ready-mix tape joint compounds.

TABLE I

UNION CARBIDE CALIDRIA ASBESTOS

Typical Product Characteristics		
	SG-130	SG-210
Reflectance (G.E. Photovolt)	68%	
Contained magnetite	2% Max.	
Alkalinity (as % of Na_2O)	0.05-0.06	
pH (5% aqueous slurry)	8.5-9.5	
Surface area (BET)	50-60 $m^2/g.$	
Oil Adsorption (DOP #/100# asbestos)	90-100	110-120
Wet Bulk, settled vol. (ml.)		
10g/250 ml./1 hr.	200	220
Dry Bulk (#/ft.^{3})	7-8	5-6
Water absorption (wt. % in filter cake)	55-60	62-65
Size distribution (Cumulative % retained)		
Wet Screen mesh size		
100	5	Trace
200	17	3
325	28-32	10-15

TABLE II

UCAR LATEX WC-130 OR 131

SUGGESTED BEDDING COAT TAPE JOINT COMPOUND

(13-DHR-18)

Ingredients and Order of Addition(a)	Pounds	Gallons	Lbs/100 Gal	% by Wt
1. Water	1932	232.43	424.16	31.39
2. CELLOSIZE TJC Thickener, Union Carbide	20	1.72	4.41	0.32
3. Bacteriastat "Dowicide" A or similar	8	0.74	1.72	0.13
4. Dispersant, "Daxad"-30, (25% ₹), Dewey and Almy	64	6.53	14.01	1.04
5. UCAR Latex WC-130, (58% ₹), Union Carbide	414	44.66	90.94	6.73
6. Dibutyl Phthalate, Union Carbide	24	2.75	5.23	0.39
7. Ethylene Glycol, Union Carbide	40	4.30	8.74	0.65
8. Calidria Asbestos SG-210, Union Carbide	180	8.45	39.62	2.92
9. Mica P-80-F, Western Mica	840	36.68	184.34	13.66
10. Clay, ASP-400, Minerals and Chemicals, Phillip	160	7.44	35.04	2.60
11. Calcium Carbonate, No. 1 White Thompson-Weinman	2468	109.20	542.17	40.11
12. NOPCO PD #1 Antifoam Nopco Chemical Company	4	0.55	0.88	0.06
	6154	455.45	1351.26	100.00

Note (a) Mixed 1.5 to 2.0 hours in a one-gallon Baker-Perkins, Sigma Blade Type Mixer, at 79 r.p.m.

Typical Properties

Water Content	35.1%
Pounds/Gallon	13.51
Brabender Viscosity	700 B.U.
Adhesion to Wallboard Tape	100%
Nailhole Cracking Resistance	99%
Sandability	Good

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TABLE III

UCAR LATES WC-130 OR 131

SUGGESTED GENERAL PURPOSE TAPE JOINT COMPOUND

(13-DHR-68)

Ingredients and Order of Addition(a)	Pounds	Gallons	Lbs/100 Gal	% by Wt
1. Water	1932	232.43	421.67	31.35
2. CELLOSIZE TJC Grade Thickener, Union Carbide	20	1.72	4.41	0.32
3. "Dowicide" A, or similar bacteriastat	8	0.74	1.73	0.13
4. "Daxad"-30, dispersant (25% T)	64	6.53	14.01	1.04
5. UCAR Latex 131 preplasticized (59% T), Union Carbide	447	48.48	97.55	7.25
6. Ethylene Glycol, Union Carbide	40	4.30	8.74	0.65
7. Calidria SG-210 Asbestos, Union Carbide	180	8.45	39.19	2.92
8. Mica, AA, Thompson-Weinman	420	18.34	91.60	6.81
9. Mica, P-80-F, Western Mica	420	18.34	91.60	6.81
10. Clay, ASP-400	100	4.65	21.71	1.62
11. Calgon, Water Conditioner	20	3.12	4.35	0.32
12. Talc, Asbestol or A-200	40	1.69	8.77	0.65
13. No. 1 White Calcium Carbonate	2472	109.38	539.69	40.13
	6163	458.17	1345.02	100.00

Note: (a) Mixed 1.5 to 2.0 hours in a one-gallon Baker-Perkins, Sigma Blade Type Mixer, at 79 r.p.m.

Typical Properties

Water Content	35.1%
Pounds/Gallon	13.45
Adhesion to Wallboard Tape	100%
Brabender Viscosity	600 F
Nailhole Cracking Resistance	95%
Sandability	Good

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TABLE IV

SUGGESTED TAPE JOINT TOPPING COMPOUND
(13-DHR-48)

Ingredients and Order of Addition[a]	Pounds	Gallons	Lbs/100 Gal.	% by Wt.
Water	1714	206.21	399.81	28.27
CELLOSIZE TJC Grade	30	2.59	6.96	0.49
Dowicide "A", Bacteriastat	8	0.74	1.84	0.13
UCAR Latex WC-130 (58% S)	345	37.26	80.47	5.69
Dibutyl Phthalate	20	2.29	4.62	0.33
Ethylene Glycol	40	4.30	9.39	0.66
Calidria SG-210 Asbestos	180	8.45	42.17	2.97
Mica (P-80-F)	100	4.37	23.36	1.65
Mica (Ser-X)	400	17.47	93.20	6.60
Clay, ASP-400	40	1.86	9.24	0.66
No. 1 White Calcium Carbonate	3127	138.36	729.53	51.56
Talcum Powder (Mallinkrodt)	40	1.69	9.24	0.66
Calgon, Regular	20	3.12	4.67	0.33
	6064	428.71	1414.50	100.00

Water Content	30.66%
Pounds/Gallon	14.14
Brabender Viscosity	840 B.U.
Adhesion to Wallboard Tape	100%
Nailhole Crack Resistance	92%
Sandability	Good

NOTE: (a) Mixed 1.5-2.0 hours in a one-gallon Baker-Perkins, Sigma Blade Type Mixer, at 79 r.p.m.

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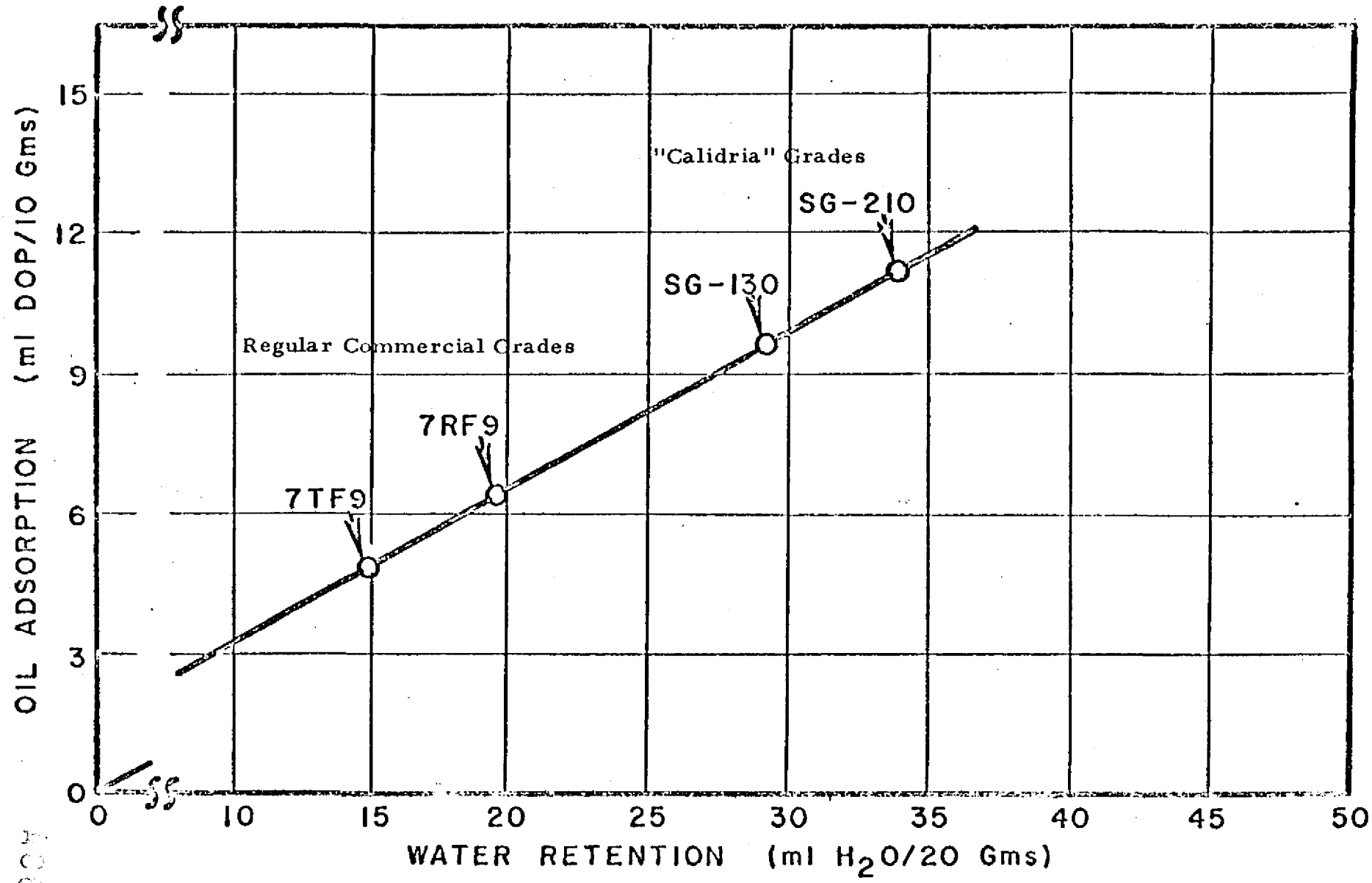
FIGURE 1



RELATIONSHIP BETWEEN WATER & OIL ADSORPTION CAPACITY OF SOME ASBESTOS PRODUCTS FOR TAPE JOINT ADHESIVE FORMULATIONS

UC 149-2

UNION CARBIDE

INTERNAL CORRESPONDENCE

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METALS DIVISION

P. O. BOX 579 · 4625 ROYAL AVE., NIAGARA FALLS, NEW YORK 14302

To (Name) Mr. R. E. Byrne, Jr.
Division UCC-Metals Division
Location Niagara Falls, NY

Date October 4, 1978
Originating Dept. "Calidria" Asbestos
Answering letter date

Copy to Messrs. G. L. Dickson
E. J. Kleber
T. P. Norris
H. B. Rhodes
[redacted]
F. J. Shortsleeve
J. E. Walsh
File

Subject Daubert Chemical

I called Bill Houghton in Oak Brook today to check on orders for RG-110-EX for Holland.

He advised me that "upper management" decided last week to discontinue all asbestos-filled products, with a target date of 12/31/78. He said this applies to domestic and export requirements and was caused primarily by union pressure at their plants and their customers. Their insurance company is also insisting that they stop using asbestos.

I told him we had a similar situation at one of his competitors, but that they were at least giving us a chance to present our side to their board of directors. I offered to do the same but he doesn't think Daubert will accept the offer.

Bill says they have substitute formulations without asbestos which are lower quality and higher cost. He also indicated their filled asphalt business was declining due to higher use of plastisol corrosion coatings which "don't contain asbestos". I chose not to correct him on this.

Daubert has been threatening to stop using asbestos for several years so this may not be the end, but this is the first time I have heard a target date.

John L. Myers

JLM:dal

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BUSINESS CONFIDENTIAL

~~DR Reb~~ - Return

cc: FHL FHL
GM File I.L.3)

PROJECT REPORT

SYNTHESIS OF DMBP SYRUP

(2,6 DiMethylol 4-t-Butyl Phenol)

AUTHORS: M. D. Bertolucci

SUPERVISOR: F. H. Ancker

DATE: May 15, 1973

PROJECT NO.: 897M14

FILE NO.: 3651

SUMMARY

DMBP (2,6 DiMethylol 4-t-Butyl Phenol) has been shown to be an excellent interfacial coupling agent for chrysotile asbestos in that its application as a pretreatment markedly improves the mechanical and the thermal stability properties of "Calidria" filled polyolefin and polyvinyl chloride composites. Pretreatment with DMBP, henceforth, enables chrysotile asbestos to be utilized as an efficient reinforcing agent in these resins, applications which so far have been limited to more expensive types of abestos (anthophyllite).

Joint studies with the Mining and Metals Division are in progress to define a manufacturing process for the direct in-line pretreatment of Union Carbide's "Calidria" (chrysotile) asbestos at King City, California. The preferred process is to add DMBP as a concentrated syrup (i.e. without isolation and crystallization) directly to the asbestos filter cake prior to pelletizing and drying.

The present report describes the reaction conditions and quality control procedures for synthesizing the DMBP syrup. This information is needed as a basis for engineering and cost studies of the integrated asbestos pretreatment process. The results of the laboratory pretreatment process and asbestos composite property studies will be presented in a separate report.

Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
Bound Brook, New Jersey

INTRODUCTION

The development of coupling agents for chrysotile asbestos based on para-alkyl phenol derivatives has been discussed in earlier reports[1,2]. Although it is feasible to apply these coupling agents as integral blend additives during compounding, it has been decided that pretreatment of Union Carbide's "Calidria" asbestos to provide a proprietary reinforcing grade of chrysotile is the preferred business option.

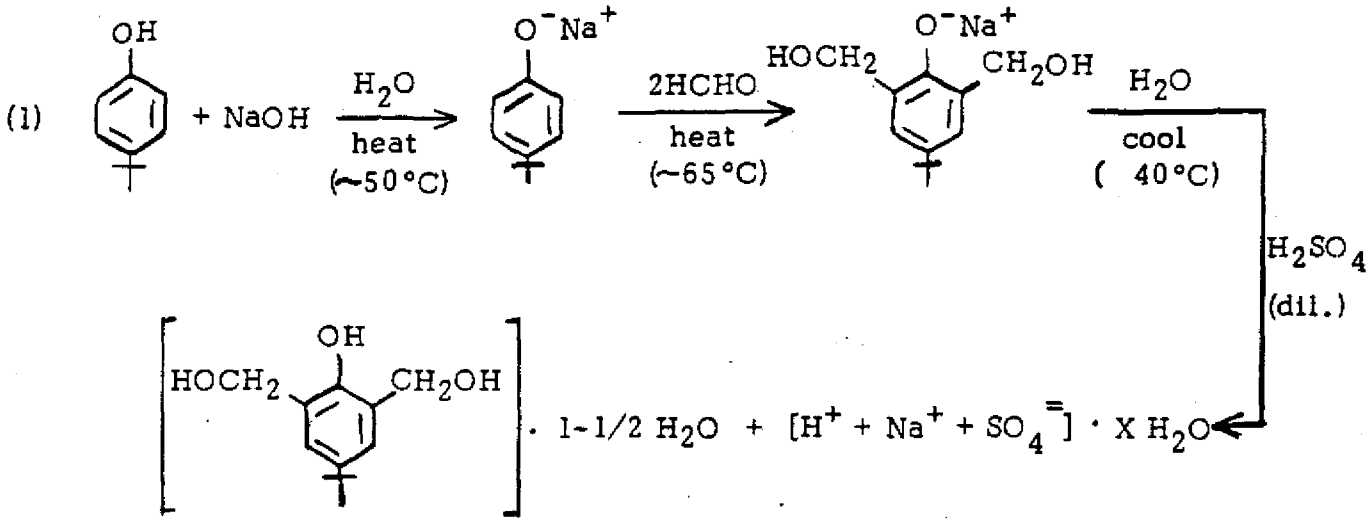
The best composite property improvements in earlier laboratory studies were obtained by pretreating the asbestos with DMBP from an acetone solution. Subsequent cooperative studies with the Calidria Group at Niagara Falls have now shown that DMBP can be added directly to the asbestos filter cake (50% H_2O) as it is prepared for pelletizing and drying in the asbestos refining process. Due to the fact that asbestos has a large surface area (~60 m^2/gm), a high level of coupling agent is required (5-10% on dry asbestos). Since chrysotile is a low cost reinforcement, the cost of the coupling agent must be as low cost as possible.

DISCUSSION

Preparation of DMBP

DMBP has been synthesized in the laboratory and in the Bound Brook pilot plant as early as 1959 in connection with studies relating to evaluations in rubber adhesives and as a crosslinking agent for elastomers[3,4]. In this process, the isolation and crystallization of DMBP are the most expensive process steps. For the purpose of asbestos pretreatment, laboratory studies show that the use of an unrefined DMBP syrup is at least equivalent to and, in many respects, preferrable to using crystalline DMBP, thus enabling considerable cost savings.

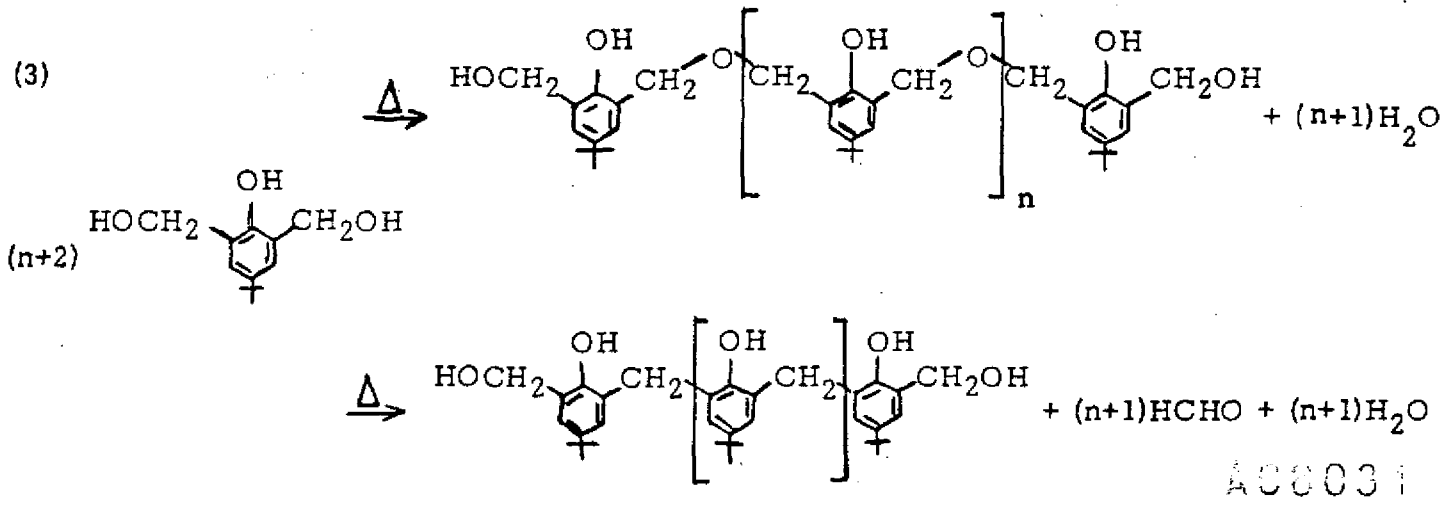
The overall production scheme of DMBP syrup can be summarized by the following reaction sequence.

(1) 

DMBP Syrup

In the laboratory preparation, 96% of the theoretical yield of DMBP was recovered as product in the form of a viscous syrup (ρ = 1.09 g/cc) which contained 10.9% water. The organic portion of this phase was found to be greater than 95% DMBP by N.M.R. analysis[5]. The aqueous phase which contains residual acid and sodium sulfate was found to retain approximately 3% syrup, which could be recovered by centrifugation. In addition, the aqueous phase contained products with carbonyl functionality to the extent of 0.07% (i.e. 1.4% based on HCHO). Thus, side reactions such as the Cannizzaro reaction which describes the disproportionation of aldehydes like formaldehyde and is illustrated in equation (2) or the thermal advancement of DMBP to higher molecular weight oligomers as shown in equation (3) do not appear to be significant under the reaction conditions described below.

(2) $2HCHO + NaOH \longrightarrow CH_3OH + HCOO^- Na^+$

(3) 

A qualitative description of the synthesis is as follows. A 22 liter reactor is charged with water, sodium hydroxide solution and crystalline t-butyl phenol. Under mechanical stirring and at approximately 50°C, Formalin is charged rapidly. Continued agitation and temperature control at approximately 65°C is maintained for two hours. The reaction medium is diluted with water and cooled to less than 40°C whence a quantity of dilute sulfuric acid is added slowly to a pH of from 4 to 5. The acidified medium is stirred for one half hour and let stand for an additional half hour. Two phases separate during this time and the product is discharged through the bottom of the reactor.

FORMULATION[6]

Reagent	Parts	Pounds	Moles
Water	142	6.6	-
Sodium Hydroxide (25% wt. NaOH) [36-E]	106	5.0	14.3
t-butyl phenol [ZZW-2514]	100	4.75	14.3
Formalin (40% wt. HCHO) [3181]	100	4.75	28.7
Water	71	3.3	-
Sulfuric Acid (30% wt. H_2SO_4)	106	5.0	13.7
Yield DMBP Syrup	149	7.1	-

Quality Control

Some care must be taken during the neutralization step as too rapid addition of acid results in a high local acid concentration which may cause resinification and subsequent globular precipitation. This occurrence however is not likely with diluted acid. Moderate temperature overshoot is not a critical factor in the usefulness of the resultant product. Extensive studies with higher molecular weight oligomers and lower molecular weight precursors to DMBP show that concentration levels under ~30% of these species do not significantly alter the material's potency as a superior interfacial coupling agent.

A simplified titration technique for product quality control is presently under investigation by F. G. Willeboordse of our Analytical Group. As an example, an appropriate method for the determination of primary alcohol with which free formaldehyde or phenolic OH does not interfere involves removing an aliquot, adding excess pyromelletic dianhydride and back titrating with caustic to a phenolphthalein visual end point. This test will be perfected as warranted.

The shelf life or thermal stability of this heat reactive phenolic monomer toward advancement does not appear to be a problem provided the pH during the neutralization step does not go below ~3.5 units by the Hydrion paper test. The advancement to 2,2' dimethylene bis(4-t-butyl phenol)ethers which occurs to approximately 10% in pH 4 neutralized syrups that stand at 30°C (86°F) for 2 months[5], does not alter the product's effectiveness in end use.

Manufacturing Process and Potential Use

The production of DMBP syrup in the light of the relative simplicity of its synthesis is open to a number of manufacturing options. Not the least important of these options involves the location of the production site. This choice must be considered in terms of the location of the raw materials, the existence of necessary production skills and equipment as well as end use at the King City mines in California. As the reaction scheme is sufficiently simple, production of the DMBP syrup directly at the King City plant should be feasible. It is possible, however, owing to a lack of available equipment at King City, that at least the initial production of the syrup for further evaluation should be run at the UCC Chemicals and Plastics plant in Elk Grove, California. The various process economics involved in these options will, of course, be critical factors in the final recommendations.

To date, DMBP pretreated chrysotile asbestos has been evaluated as a reinforcing filler in polyolefin and polyvinyl chloride resins. Evaluations of this material will be extended to other thermoplastic resins as well as to polyester (thermoset) resins; the latter of which represents a significantly larger potential market. These studies will help define the potential net volume requirements for this product.

ACKNOWLEDGMENTS

I wish to thank A. C. Soldatos for enlightening discussions and access to his prior art. Also, I wish to thank R. G. Azrak for his counsel and R. G. Wolf for his excellent technical assistance.

M. D. Bertolucci

M. D. Bertolucci

MDB:bcc

Notebook Reference: 10168

Date Received: May 7, 1973
Date Typed: May 11, 1973

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