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PROJECT REPORT

SYNTHESIS OF DMBP SYRUP

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

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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.

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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

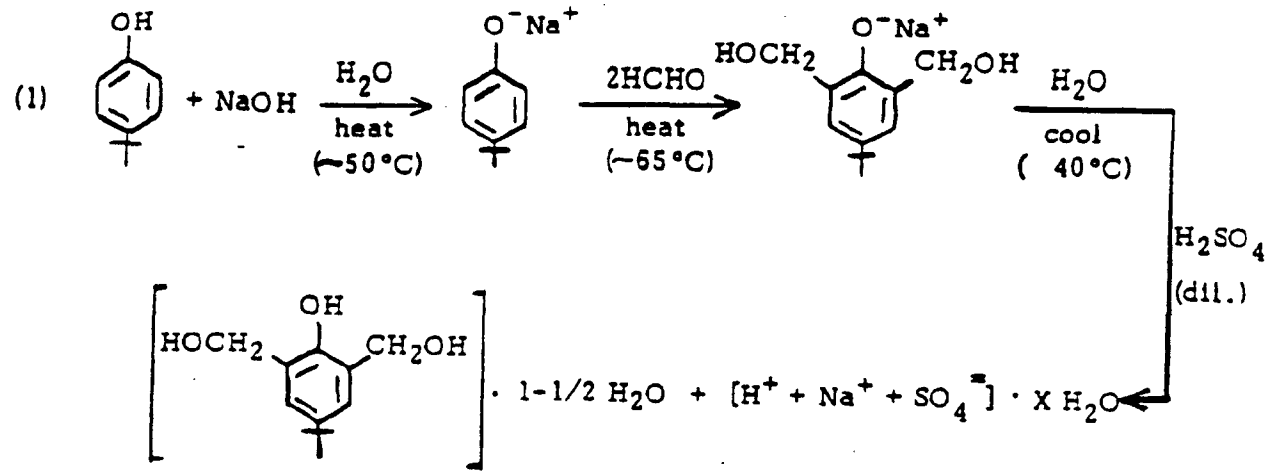
Preparation of DMBP

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.

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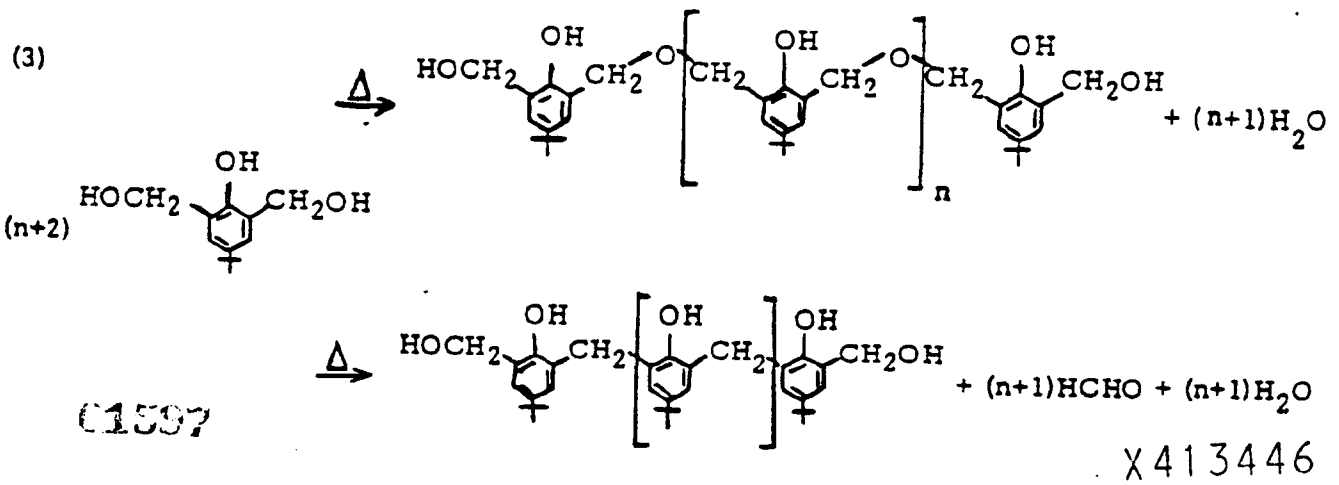
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DMBP Syrup

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) 

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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	-

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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.

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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.

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M. D. Bertolucci

MDB:bcc

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