

# UNITED STATES PATENT OFFICE

2,283,900

## PROCESS FOR PRODUCING RESINS OF THE SULPHUR DIOXIDE-OLEFIN TYPE

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No Drawing. Application February 7, 1939,  
Serial No. 255,051

10 Claims. (Cl. 260-94)

This invention relates to resins of the sulphur dioxide-olefin type and to new and improved processes for producing them.

It has long been known that resinous polymerization products may be produced under proper conditions by the reaction of sulphur dioxide with active unsaturated organic compounds of the olefin type, of which the mono-olefins like ethylene, propylene, butene-1, butene-2, isobutene, pentene-1 and pentene-2 are examples. Other examples of such unsaturated compounds are butadiene, pentadiene and other conjugated diolefins; pentyne-1, hexyne-1 and other acetylenes; and polyfunctional unsaturated compounds of the nature of allyl alcohol and allyl ethers.

This polymerization reaction is usually carried out with an excess of sulphur dioxide in a sealed glass tube or steel bomb, at comparatively low temperatures and in the presence of a catalyst. Among the catalysts which have been proposed heretofore are light of the proper wave length, oxidizing compounds such as certain peroxides, nitric acid and silver nitrate, and certain organometallic compounds, such as tetraethyl lead.

The commercial development of sulphur dioxide-olefin resins has been hindered by the lack of catalysts of sufficient activity. Most of the known catalysts require many hours and even days to complete the polymerization to a point giving a practical yield of resin, and in many cases the resinous product is contaminated or discolored to such an extent, or has such an undesirable physical condition, that it possesses little or no practical value for use as a moulding material, as a base for lacquers, etc., or as a plastic in other fields.

A catalyst that has been considered desirable for bringing about the reaction between sulphur dioxide and olefins is the naturally-occurring terpene peroxide, known as ascaridole. When using ascaridole, good yields of polymer can be obtained in a fairly reasonable time as compared with other known catalysts; for example, yields of as high as 85% are obtainable within an hour and a half when producing butene-1 resin. On the other hand, the use of ascaridole according to known processes does not give nearly as rapid production as desired for commercial operation, and the product of the reaction is discolored to an objectionable extent and very difficult to convert to a useful physical condition. Furthermore, the catalytic activity of ascaridole, when used according to prior processes, seems to be relatively high only when a considerable excess of sulphur dioxide is present in the reaction mix-

ture. This fact leads to difficulties in purifying the resinous product.

An object of my present invention is to provide an improved process for producing resins of the sulphur dioxide-olefin type by which the speed of the polymerization reaction is greatly increased.

Another object is to provide a process giving an increased yield of resin and reducing the amount of reaction mixture which must be handled per unit weight of product.

A further object of my invention is to provide a process which produces sulphur dioxide-olefin resins having improved physical characteristics.

Other objects and advantages of the invention will become apparent from the following description.

I have discovered that the polymerization reaction between sulphur dioxide and active unsaturated compounds of the olefin type may be tremendously accelerated by carrying out the reaction in the presence of terpene peroxide and small amounts of halogen acid. When using my improved process the speed with which the reaction takes place is greatly increased, and the reaction time is greatly reduced.

According to the preferred embodiment of the invention, the reaction is carried out in the presence of ascaridole, a naturally occurring terpene peroxide that is readily available, and halogen acid.

Optimum results are secured by using ascaridole and hydrogen chloride. Other halogen hydrides, such as hydrogen fluoride and hydrogen bromide, may be employed, but to somewhat less advantage. Hydrogen iodide is the least effective.

An important feature of the new process consists in its utility when used in conjunction with the process disclosed in the copending application of R. C. Hills and myself, Serial No. 257,336, filed Feb. 20, 1939. According to an embodiment of that process, the reaction between sulphur dioxide and olefin is carried out in the presence of an excess of the olefin, with or without an additional solubility regulator, such that the molar ratio of solubility regulator to sulphur dioxide in the reaction mixture is preferably at least 3 to 1. A granular resin that is easy to wash is obtained from this reaction. In the practice of said embodiment, using known catalysts, it has been difficult, if not impossible, to obtain yields higher than 30-40% of the theoretical yield. On the other hand, when using ascaridole and halogen acid as the catalyst in a reaction mixture containing a large excess of olefin, ac-