The Preparation of Standoil With a Catalyst

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EXPERIMENTAL work conducted before World War II has shown that sulfur dioxide acts as a catalyst for the shifting of double bonds in those systems where two double bonds are separated by a single methylene group. Thus it is possible to prepare an oil which contains conjugated double bonds from linseed oil. This oil has been called activated linseed oil. A further continued heating causes polymerization and thus has become a base for a catalytic process for the production of stand oil. The activation was patented during the war (1) while the polymerization process had been patented previously (2). In either case the reaction products are practically free from sulfur.

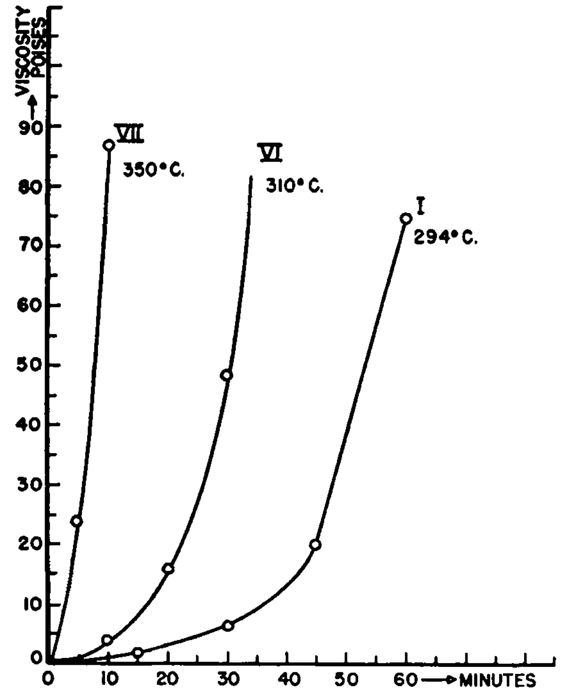

FIG. 1.

Although more recently other catalysts are mentioned in the literature, the sulfur dioxide process has now been used in practice, among others, by the Dutch firm, P. Schoen en Zn., Zaandam, Holland, which works under a license from the Imperial Chemical Industries W.I.S. process. A paper by D. Cannegieter (3) has appeared, reporting that the process can be readily controlled in practice. It is said to be possible to predict how long it will take to obtain a standoil of any desired viscosity.

Although a theory of the cause of catalytic activity of sulfur dioxide has been published by one of the authors in collaboration with J. H. de Boer and J. P. W. Houtman (4), much work remains to be done on the polymerization process. If the industrial results are compared with earlier laboratory experiments, it is observed that the W.I.S. process proceeds more slowly than would be expected from the laboratory results.

The cause of this discrepancy is the poor contact between the oil and the sulfur dioxide. This was to be expected because in the factory batch, not continuous, operation was employed. Sulfur dioxide was introduced by a tube while in the laboratory experiment a very effective stirrer was used.

It is possible to decrease the time of the reaction considerably by working at higher temperature (Fig. 1, Table I).

TABLE I

Temperature	294°	310°	350°
Time in min.	45	25	5
Viscosity in poises	20.1	27.0	24.2
Acid Value—mg. KOH/g.	5.4	6.3	12.5

These are laboratory experiments in which a bell-stirrer was used. The favorable effect of higher temperature, 310° and 350° respectively, is clearly shown. In the experiment at 350° a viscosity of 20 poises was obtained in 4½ minutes. At higher temperature the acid value increases more rapidly than at 290°C. This need not be an objection because some acid content may be desirable to promote the wetting of the pigments.

The problem which had to be solved was the preparation of a standoil at the same rate as in earlier experiments. Also it was desirable to use a continuous process. Since intensive mixing of the sulfur dioxide and the oil was necessary, use of a tube heater was indicated.

The apparatus used is shown in Figure 2. The oil in the coil was preheated in Bath B and then thoroughly mixed with sulfur dioxide in vessel D by means of a bell-stirrer. The foam thus obtained was conducted in a second coil, heated in Bath E. The catalytic polymerization proceeds readily with good contact and high temperature. The reaction product must then be separated from the catalyst. This can be done by applying vacuum, which also eliminates many of the volatile decomposition products present in the oil.

The oil is drawn from the mixing bath D through the coil to the receiver F. The coils used in the apparatus were of aluminum. The internal diameter was 10 mm., the external 12 mm. The length of both coils was 3 meters, of which 2 meters were exposed to the preheating in Bath B and Bath E (contents of the latter coil 236 ml.).

The volume of the oil in the mixing vessel D, which is kept at constant level, is about 150 ml. About 3.6 liters of standoil are obtained in the receiver per hour, or a daily capacity of 90 liters. The mixing vessel is emptied every 2.4 minutes. This time is sufficiently long that at high temperatures some polymerization occurs in the mixing vessel.

In the reaction coil, in which the temperature was much higher (350-360°C.) than in the experiments described in earlier papers, the oil remains about 4 minutes. The total reaction time is therefore 6 to 7 minutes for the preparation of a standoil with a viscosity of about 20 poises at 20°C. The calculation

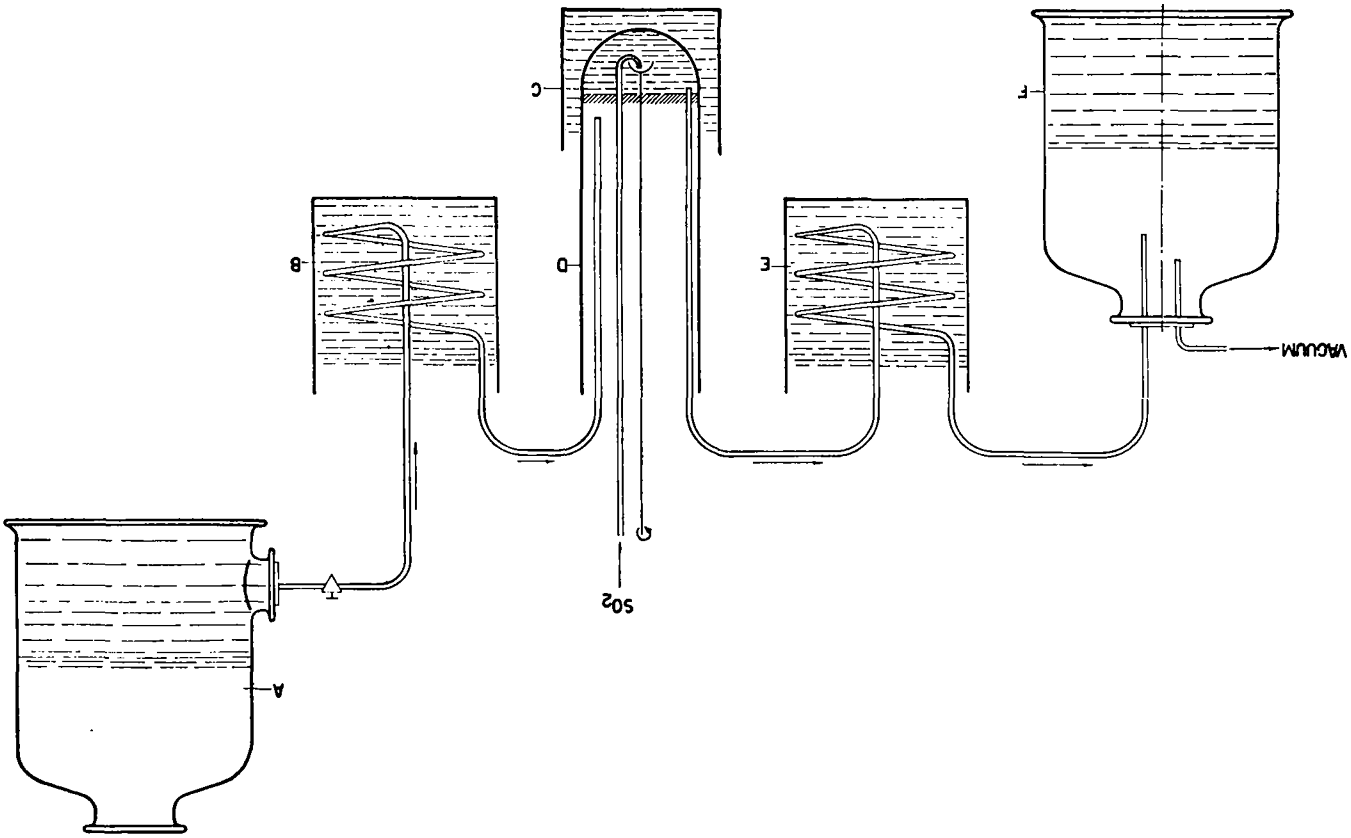

FIG. 2.

of the reaction time is not entirely correct, the reaction coil not being filled with oil but with foam (oil and sulfur dioxide). This coil should be filled with foam. Therefore the real time of contact in the reaction coil is shorter, the polymerization in the mixing vessel relatively becoming more important.

Under the conditions mentioned in this paper, working continuously and heating in coils at 350-360°C., the acceleration is very pronounced; see Table II.*

TABLE II

Catalyst	SO_2	SO_2	....	....
Temperature in Bath C....	360°C.	345-350°	345-350°	345-350°
Temperature in coil (Bath E)........................	355	360	360	360
Duration of run in min...	....	24	56	26
Quantity of oil in ml........	....	980	1070	1120
Ml./min.............................	53	41	19	43
Refractive index 20°C......	1,4906	1,4904	1,4882	1,4864
Viscosity in poises 20°C...	22.5	29	17	8
Iodine value......................	119	118	122	135
Acid value.........................	16.0	11.6	13.4	9.7

The properties of oils, bodied at high temperatures in the presence of sulfur dioxide, are as follows:

Refractive index..	1,4906	1,4916	1,4901
Viscosity in poises......................................	22.5	40.0	21.8
Iodine value...	119	109	119
Acid value..	16.0	15.2	13.7

The oil bodied at high temperature is clearer than the oil treated at 290-300°C. and shows no settlings. The drying time is somewhat longer than with oil bodied at 290°C., but it dries tackfree in about five hours when the usual driers are added.

The properties are compared by making different paints and exposing them on the roof. After one year's exposure no essential differences can be seen between an oil bodied at 360°C. with sulfur dioxide in coils and oil obtained by the batch process at 290°C. in the absence of sulfur dioxide.

The use of aluminum as a material of construction for the preheating and for reaction coils cannot be recommended. The tubes were mechanically not very strong; also there was some corrosion although apparently by covering the surface of the metal, the corrosion was noticeably less. In the future the use of chrome steel or copper might be recommended. Further investigations in this respect are necessary. Also the heating baths might be united.

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* Some of these experiments were carried out by J. L. Oudesluijs.