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POLYMERISATION OF ETHYLENE UNDER HIGH PRESSURE.

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Polymerisation of ethylene under high pressure has long been studied fair widely. But generally, as it was carried out under relatively low pressure i. e. <500 atm. and relatively high temperature i. e. $200\sim400$°C, the product was a gaseous, liquid or semisolid, substance of lower polymerisation.

Fawcett, Gibson, Perrin and others have lately stated1) that a solid, tough polymer can be produced from ethylene by an application of higher pressure, such as $1000\sim3000$ atm.

However, such a kind of research under high pressure is not achieved successfully in our land and that such a kind of polymer has come to be demanded urgently for a special use. Therefore, we set about an investigation of it in December, 1943 and succeeded in producing a solid polymer of ethylene well possessed of required properties in March, 1944. We started, with the result of further examination, an operation of a pilot plant for the production in December, 1944.

And yet, the research was rough and ready and not investigated minutely enough, as it was hurried recklessly for the production in the war. So that, we desired to continue further investigation. But the apparatus was destroyed unfortunately by an air raid and the research is suspended now. But it will be resumed before long and the whole result will be reported in detail.

Here, however, the result of the experiments executed hitherto is briefly summarized.

Apparatus and Operation.

A diagram of the experimental apparatus is shown in Fig. 1, where 1-alcohol dropping apparatus; 2-vaporizer of alcohol; 3-catalysation tower for dehydration of alcohol; 4-purification apparatus of ethylene, 5-gas tank; 6-compressor; 7-liquefaction apparatus of ethylene, 8-preliminary compressor of the reaction vessel named fore-compressor; 9-reaction vessel.

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1) E. W. Fawcett, R. O. Gibson, M. W. Perrin and others, B. P., 471, 590 (1939). F. P., 817, 374 (1937). U.S.P., 2, 153, 553 (1939), U.S.P., 2, 188, 465 (1940).

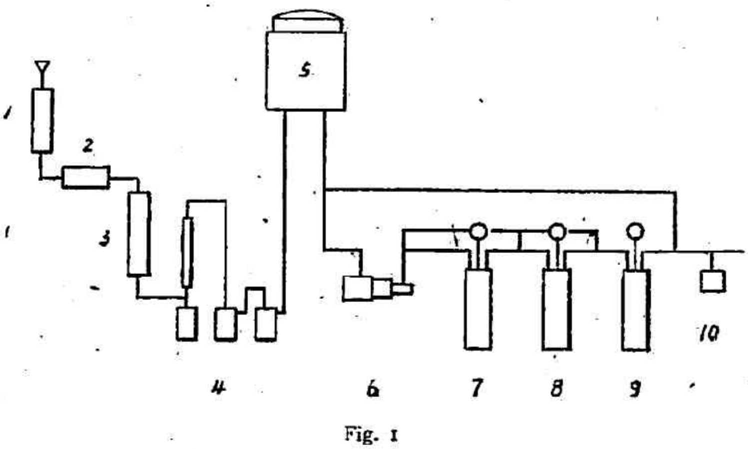

Fig. 1

The liquefaction apparatus consists of a cylinder of about 4 liter, which can be cooled with liquid air or brine.

The reaction vessel is a thick cylinder of Ni-Cr-steel, whose inner diameter is 4.5 cm and its capacity is about 520 c.c. and it is durable for high pressure of 3000 kg/cm^2. This reaction vessel is furnished with a kind of intensifier named forecompressor here.

The said forecompressor is also a similar cylinder with a diameter of 3.5 cm., capacity of about 450 c.c. and durability for 2000 kg/cm^2. It is connected to a high pressure source of gas or liquid and is able to intensify the pressure of the reaction vessel to a certain degree by means of the high pressure gas or liquid.

Preparation of ethylene—Ethylene is obtained by the dehydration of ethylalcohol with alumina and purified with pyrogallol, sulphuric acid and alkali. The pyrogallol was replaced with a Cu-NH_3-solution in the later experiments.

The ethylene thus prepared is about 97.5 ~ 99.4%, containing 0.06 ~ 0.02% of oxygen.

Charge of ethylene to the reaction vessel—In order to obtain a sufficient high pressure in a reaction vessel, ethylene gas is to be charged in a compressed state. Here are two methods for the purpose, that is, ethylene is charged in a gaseous state directly by a compressor, which is generally utilised, or it is charged in a liquid state. The latter method is taken up here. The liquid ethylene in the liquefaction apparatus is led to the reaction vessel and the forecompressor. Then the reaction vessel is forced to charge much more by means of the forecompressor to a degree sufficient to get a required high pressure at a certain high temperature.

A set of these apparatus including the liquefaction apparatus, the forecompressor and the reaction vessel is especially designed for the charge of ethylene and has another important agent to purify ethylene during its operation of charging[2].

Ethylene charged in the reaction vessel in such a manner amounts to about 270～290 gr.

Polymerisation—After the charge is ended the reaction vessel is sealed and heated in an electric furnace to a temperature where ethylene begins to polymerize.

Experimental and Results.

1) Experiment for a production of a solid polymer.

It was examined whether a solid polymer as shown in the lilerature could be obtained with the aforesaid apparatus. At first a pressure charge of pure ethylene is measured for the temperature and it is found that the P-T curve has a point of inflexion at a temperature of about 160°C and the pressure ceases to increase at about 220°C. Therefore, we started the experiment marking these temperatures. The first 10 experiments scarcely get to a gratifying result.

But in experiments NO. 11 and 12 a fairly satisfactory product was obtained, a white spongy mass of 63 gr. and 93 gr. respectively.

Fig. 2. shows timely change of pressure and temperature in the experiment NO. 11.

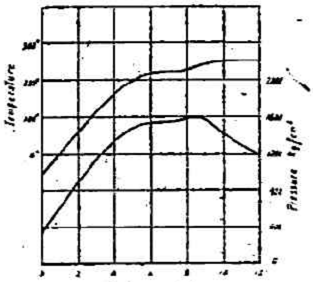

Fig. 2 (Exp. 11)

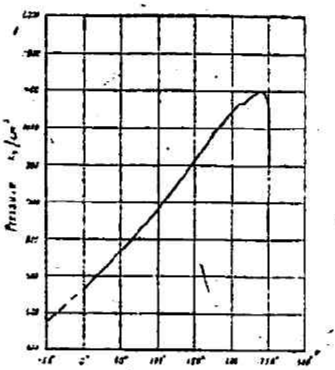

Fig. 3 (Exp. 11)

It takes about 5½ hours to raise the temperature of the reaction vessel to 220°C, where the pressure scarcely increases. At 245°C the pressure begins to decrease and with further temperature rising it gradually becomes rapid, say, about 150 atm. during the first 1 hour, so that the temperature is held constant at 251°C.

Fig. 3 shows the P-T curve of ethylene in the polymerisation. It has a maximum pressure of about 1600 atm. at 245°C and a point of inflexion about

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[2] This apparatus and operation is registered as a patent in January 1945.

160°C, which is considered to be caused by the beginning of polymerisation; although it is very slowly done there. A break at 220°C is owing to the constant temperature held at that point as is seen in Fig. 2, because the reaction is already in progress there.

Now, the products in these cases are both white spongy masses and melt at about 107°C and 110°C respectively and can be spun to fine kinds of thread or moulded to white wax like tough rod or plate and have superior electric properties sufficient for use. Therefore, they are taken as a certain standard of the product in the present research.

2) Experiment with coarse ethylene.

A roughly purified ethylene was used for trial. In this case, ethylene is contained 97.5~98.5% and oxygen about 0.05~0.06%. For example, the results of experiments NO. 17 and 21 are shown in Figs. 4, 5 and 6, 7.

In experiment NO. 17 (Fig. 4, 5) occurred an explosion at the end of reaction

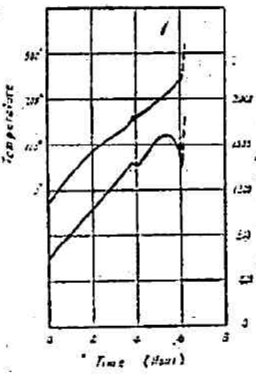

Fig. 4 (Exp. 17)

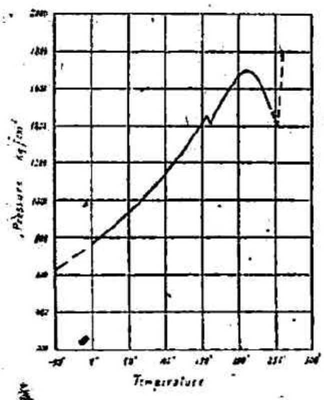

Fig. 5 (Exp. 17)

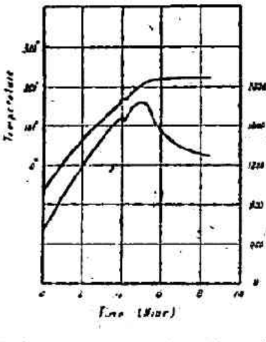

Fig. 6 (Exp. 21)

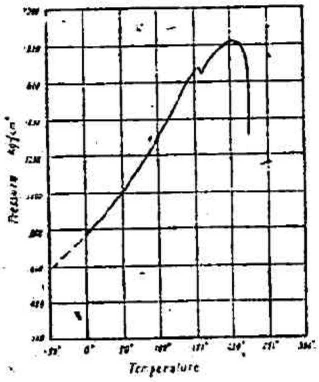

Fig. 7 (Exp. 21)

and ethylene was wholly carbonized. The explosion in this case is considered to be caused by a rapid heating and no controll of temperature rather than an excess of oxygen as is seen in Fig. 4. In experiment NO. 21 (Fig. 6, 7), therefore, a precaution is taken for that point and successfully obtained an acceptable product of white mass of 81 gr. which melts at 110°C and has an alike properties as above.

Now, it is interesting to mention that in Figs. 4 and 6 a conspicuous pressure fall is observed on the pressure curve at a temperature about 160°C which corresponds to the point of inflexion in the previous case (Fig. 3) and that a clear heat toning at that point in the temperature curve respectively. This means obviously an occurrence of a new type of polymerisation caused by an excess of oxygen and it may be different in a mechanism of the reaction from the following reaction at higher temperature, as it is transient and has no continuity to the latter.

3) Experiment for earlier polymerisation.

As in the previous cases an excess of oxygen gives rise to a new type of polymerisation early at a lower temperature, so some experiments were executed especially with more oxygen, i. e. $> 0.06\%$. But the reactions in these cases are apt to explode and the more the oxygen, the more excessive the aptitude.

An example is shown with the result of experiments No. 28 and 30 in Figs. 8, 9 and 10, 11 respectively.

In experiment NO. 28 (Fig. 8, 9) the temperature and the pressure, which were very slowly increasing up to about 120°C, were inclined to increase abruptly, so the temperature was controlled to be constant at 125°C taking precaution against an explosion, while the pressure rapidly decreased. The product in this case is a yellow spongy mass of 16 gr. which melts at 113°C.

In experiment NO. 30 (Fig. 10, 11) a rapid heating and no controlling led

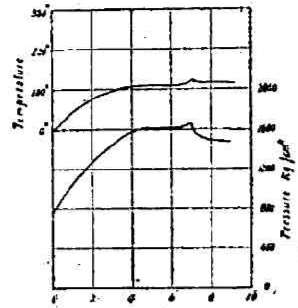

Fig. 8 (Exp. 28)

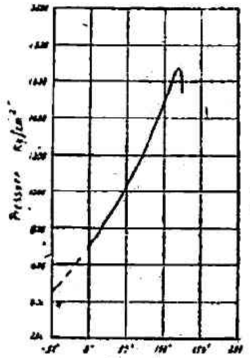

Fig. 9 (Exp. 28)

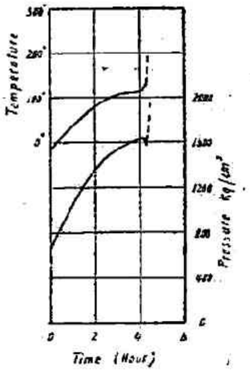

Fig. 10 (Exp. 30)

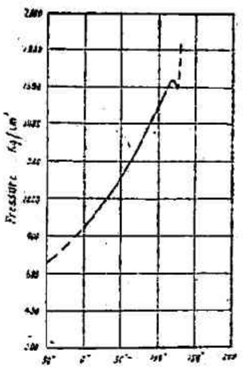

Fig. 11 (Exp. 30)

the reaction to an explosion. However, in this case the product remained uncarbonized and a yellow melted mass of 15 gr. was obtained which melted at 110°C.

A striking fact is that a reaction occurs anew in these experiments earlier at a lower temperature of about 120°C from the previous cases. The phenomenon is to be investigated with much interest, but it was withheld a while, because the product in this earlier reaction is relatively small and yet its properties are not adaptable for the present use.

4) **Experiment for formal reaction.**

The foregoing experiments show that a fine polymer of high quality is produced when it is operated with a formal reaction at higher temperature than 160°C with ethylene purified to a certain degree, i. e., >98.5% ethylene, <0.05% oxygen.

The experiment for the purpose was carried out about 45 times and an example of the results is shown in Figs. 12, 13; 14, 15 and 16, 17 with experiments NO. 57, 58 and 60 respectively.

Fig. 12 (Exp. 57).

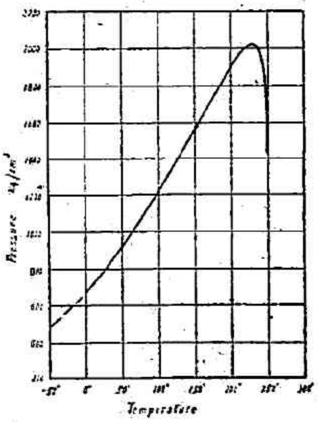

Fig. 13 (Exp. 57)

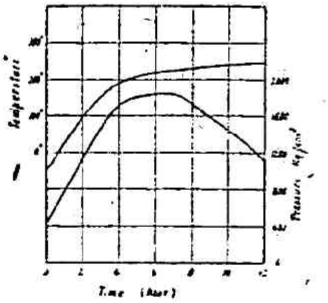

Fig. 14 (Exp. 58)

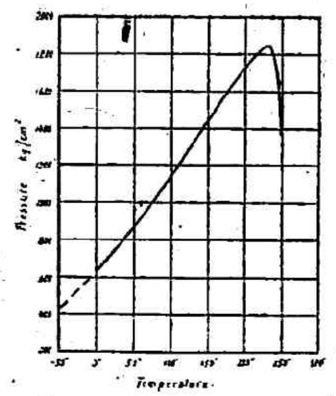

Fig. 15 (Exp. 58)

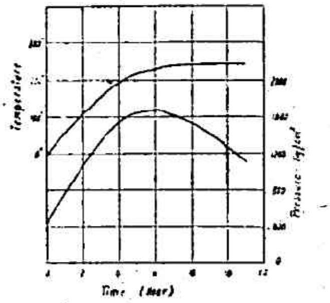

Fig. 16 (Exp. 60)

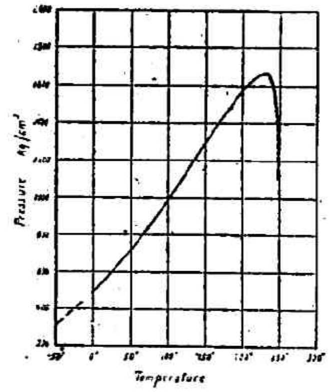

Fig. 17 (Exp. 60)

As is seen the curves in these figures are quite similar to one another, only being different in the maximum pressure i. e. about 2020 atm, 1840 atm and 1680 atm in order respectively caused by the amount of ethylene charged in the reaction vessel. The products of these experiments are all white spongy mass quite similar to that of experiment NO. 11 (Fig. 2, 3). The yield is 97 gr, 81 gr and 75 gr which melts at 110°C, 107°C and 104°C in order respectively. The other physical properties are also alike to that of experiment NO. 11 on the whole, but somewhat degraded in their order. For example, the value of tan δ in electric properties is 3, 6 and 10 in order respectively.

5) Experiment for retardation of reaction.

In case an excess of oxygen is contained in ethylene or the temperature controlling is not well operated, a reaction is apt to explode and yet a restriction of this kind is somewhat difficult in practice. Therefore, a retardation of the reaction velocity comes to the point and a dilution of ethylene with a non reacting gas such as nitrogen, ether, carbon monoxide and the like is adaptable for the purpose.

Nitrogen is taken up here for the example.

A charge of nitrogen is as follows—after liquefied ethylene is charged in the reaction vessel, it is forced to charge further with compressed nitrogen to such a degree as the nitrogen content is fitted to a desired amount. As an example, the results of experiments NO. 82 and 83 are shown in Figs. 18, 19 and 20, 21.

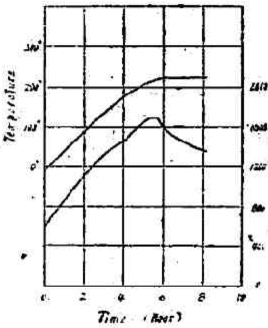

Fig. 18 (Exp. 82)

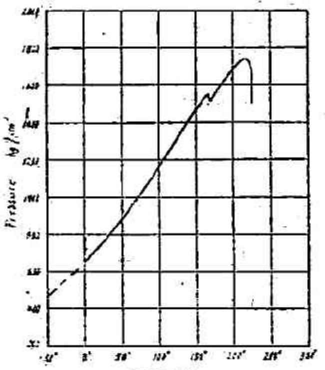

Fig. 19 (Exp. 82)

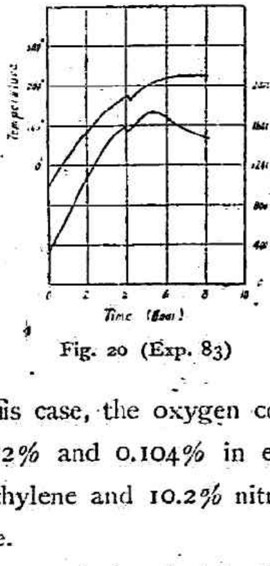

Fig. 20 (Exp. 83)

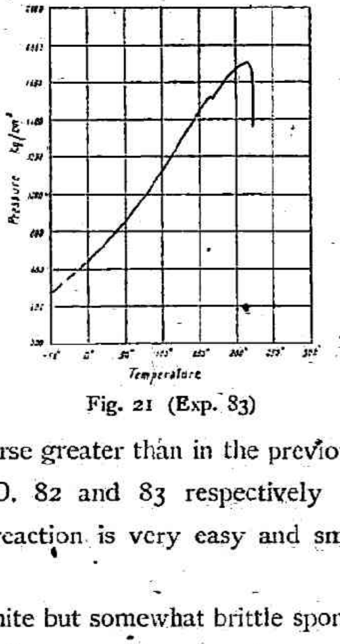

Fig. 21 (Exp. 83)

In this case, the oxygen content is of course greater than in the previous cases, i.e., 0.072% and 0.104% in experiments NO. 82 and 83 respectively for both 89.4% ethylene and 10.2% nitrogen, yet the reaction is very easy and smooth on the whole.

However, the product in this case is a white but somewhat brittle spongy mass of 45 gr and 55 gr respectively which melt both at 104°C and not so acceptable in other physical properties.

Further investigation is also required for it.

Consideration of Result.

The experiment was executed about 100 times under various conditions and it was concerned with each operater and his assistants by turns. Therefore, personal errors in various measurements can not be avoidable to some extent, and so that, strictly speaking, a certain reexamination is necessary for a special part of the result.

A solid tough polymer of ethylene possessed of a required physical properties can be produced fair contentedly by such a method as in the present research. As for the operating conditions, the higher the pressure, the better the properties of a product. But a pressure over 2000 atm. is not so preferable in practice now. For an oxygen content in ethylene, the more the content, the easier the reaction, but an excess of oxygen over a certain limit of about 0.05% affects the reaction and leads it nearly to explosion and that it gives an unacceptable quality to a product. Therefore, a suitable condition is a pressure of abuot 1600 ~ 1800 atm., temperature of about 230 ~ 250°C and the oxygen content of about 0.02 ~ 0.04%.

Now it is recognized that there are three kinds of reactions in the polymerisation of ethylene, under high pressure. The first occurs at about 120°C as is seen in Figs. 8, 9 and 10, 11. It is a transient, but fairly active reaction and is quite an exceptional one, being not recognized hitherto. The second occurs at about 160°C as shown in Figs. 4, 5; 6, 7; 18, 19 and 20, 21. It is generally observed when oxygen content is in excess and the more excessive the more active it is. It is also a kind of passing phenomena having no continuity to the following formal reaction.

The last formal reaction occurs at about 210° ~ 250°C and that it is classified further in two types. The one arises at about 210°C and becomes fairly active at about 220°C, reducing gradually with constant temperature of about 225°C. This certainly occurs in case oxygen content is in excess and the reaction is accompanied with the second reaction as is seen in Figs. 4, 5; 6, 7; 18, 19 and 20, 21. The other arises at about 230°C somewhat higher than the previous case and proceeds slowly, becoming gradually active with a temperature rising up to about 250°C. This occurs certainly in case oxygen content is very small and the second reaction is not recognized preliminarily, as in Figs. 2, 3; 12, 13; 14, 15 and 16, 17.

These phenomena are obviously effected by the oxygen contained in ethylene and a role of oxygen in the reaction is quite a matter of interest.

The problems will be discussed in the following report.

This research was carried out in the dispatched laboratory of Noguchi-Institute to Minamata and co-operated by A. Horiuchi, H. Fuzii, T. Watanabe, M. Tsuda, K. Mori, Y. Umemura, R. Aoki and I. Fuchizaki, the fellow of the Institute at that time.

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