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MISCELLANEOUS CHEMICALS
I.G. FARBENINDUSTRIE A.G.
LUDWIGSHAFEN AND OPPAU

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

Ludwigshafen's capacity for Igamids totaled 300 tons per month. They also produced hexamethylene diamine for the Desmophens (Igamide U) produced at Leverkusen. Since this development was quite new, production had attained a rate of only 20 tons per month. Ludwigshafen believes that Igamide U is better than A in that it has lower water solubility, better oxygen resistance and better electrical properties.

Details on the production of adipic acid and hexamethylene diamine were not obtained. Adipic acid was made from cyclohexanol using two different processes - the conventional nitric acid oxidation step, and catalytic oxidation with air (oxidation of cyclohexanol to cyclohexanone over a silver catalyst, then oxidation to adipic acid using manganese acetate catalyst.)

e. Polyethylene (Lupolen)

Two grades of polyethylene were produced at Ludwigshafen:

Lupolen N - a low molecular weight product, about 2000 to 3000 on the Staudinger scale, tested in a decalin solution, and

Lupolen H - a high molecular weight compound, about 20,000.

Both products were made by continuous high pressure polymerization of pure ethylene. Data were given by Dr. Hopff.

(1) Lupolen N

In preparing Lupolen N, ethylene was compressed to 200 atmospheres and pumped as a liquid into a pipe coil type polymeriser along with a solution of methanol containing about 0.6% benzoyl peroxide catalyst which was equivalent to ten percent catalyst based on the polymer formed. The reactor consisted of 40 meters of jacketed pipe 3 cm I.D. arranged in a number of sections so that independent temperature control could be obtained. The initial temperature, in the first steam heated section, was 110°C. The intermediate sections were water cooled in order to maintain the temperature at 100-120°C while the lower discharge end of the reactor was maintained at 150°C in order to keep the polymer sufficiently fluid. The reaction mixture leaving the coil contained about 79% methanol, 15% unreacted ethylene, 5% polymer and about 1% of by-products from the catalyst. It was discharged into a tower and maintained under slight pressure at 130°C to keep the methanol in the liquid state. The molten polymer, which is insoluble in methanol, collected in the bottom of the tower and was drawn off periodically to a cooling pan. The liquid methanol layer was expanded to atmospheric pressure, flash distilled to remove traces of polyethylene, benzoic acid etc. and then recycled to the system. The effluent ethylene gas was scrubbed with sodium hydroxide to remove formaldehyde and was then recycled to the compressors.

Conversion to polymer was about 20-25% per pass.

The polymer product drawn off was given a final treatment by blowing with a current of nitrogen for 15 minutes at 130°C in order to eliminate traces of contained benzoic acid. The resulting product having a melting point of 106°C and the consistency of paraffin oil when molten, solidified to a brownish hard wax which was blended with Oppanol B for preparation of cable dopes, to yield a mixture containing only 10 to 25% of the pure Lupolen H. Some uses were found also in the preparation of polishes for furniture, floors, etc.

The yield on ethylene was better than 90%; in some trials when gas leakage was minimized a yield as high as 96% was obtained. Methanol losses were high, about 10% to 25% of the polymer formed.

Because of the corrosive nature of the by-products, the entire equipment was constructed of stainless steel.

A unit of the size described with a capacity of 10-15 tons of polymer per month was built at Zweckel from pilot plant data obtained in tests at Ludwigshafen.

(2) Lupolen H

The preparation of Lupolen H was carried out in a similar manner, but at much higher pressures and in absence of solvent.

Ethylene was compressed first to 300 atmospheres and then to 1500 atmospheres. Traces of oxygen were added as a catalyst using 0.05 to 0.10% based on the ethylene charged. Since the amount of oxygen was very important, a special control unit was designed. A portion of the feed mixture was withdrawn, mixed with a metered quantity of nitric oxide, NO, and then passed through a test cell located in a circuit containing a photoelectric cell. Oxygen reacted with the NO to produce brown nitric oxide the concentration of which was measured by the photo cell. Automatic control was arranged to hold the oxygen content at a predetermined level. It was stated that the unit was accurate to 0.001% oxygen in the feed gas.

The reactor proper consisted of a pipe coil 80 meters long by 16 mm ID (the discharge end was enlarged to 20 mm to permit ready discharge of the viscous polymer). At the entrance end of the coil the temperature was raised to 220°C. As soon as this temperature had been reached to initiate the reaction, cooling was applied to control the heat of reaction, maintain the temperature at 180-200°C in the bulk of the coil and finally deliver the discharged product at a temperature of about 130°C. The polymer syrup leaving the coil, at 130°C, passed through a manually operated control valve where the pressure was released and the product discharged to a receiver. Molten polymer collected in the receiver was withdrawn periodically and cast in pans.

Conversion to polymer was only 10% per pass since a poor polymer of yellow color resulted if the reaction was carried too far. The ethylene leaving the receiver contained formaldehyde, formed almost quantitatively by the oxygen introduced as a catalyst. This gas was scrubbed with NaOH by passing in series through two towers, and was then returned to the compressors for recycling.

Typical feed gas contained:

Ethylene	96.8%
Ethane	1.8
Acetylene	0.1
Oxygen	0.3
Nitrogen	0.9

The oxygen concentration was lowered automatically by the reaction as described above. Recycling of the ethylene was continued until the ethylene concentration was reduced to 90% C_2H_4 at which time the gas was vented.

The product which was recovered as a pure white solid was used primarily for the production of materials for use in electrical insulation particularly for high frequency work. Military demands consumed the bulk of the production. For most uses the polymer was used as is. In special cases where a softer material was required about 10% Oppanol B was blended. This is the only known plasticizer which does not seriously reduce the good electrical properties of polyethylene.

The capacity of the plant described above was 2 to 5 tons per month. The Ludwigshafen plant was damaged badly and a new unit was recently erected in Gendorf. However, this had not yet come into production. Dr. Hopff made the following additional interesting remarks on polyethylene in general.

X-ray studies have shown that the polyethylene is a straight chain polymer. They have done no work on the preparation of short chain polymers of low chain length, say in the C_{20} range.