

## Emulsion Polymerization of Ethylene.

### I. Polymerization Formulas and Conditions

ARTHUR F. HELIN, HARRY K. STRYKER, and GERALD J. MANTELL, *Research Center, Spencer Chemical Division, Gulf Oil Corporation, Merriam, Kansas*

#### Synopsis

Formulas and operating conditions for the emulsion polymerization of ethylene are described. Stable latex products were obtained with a variety of anionic and nonionic emulsifiers, but for the majority of the work fatty acids or polyethoxylated alkyl phenols were used. Potassium persulfate was a satisfactory initiator at concentrations of 0.05–0.50 part per 100 parts of aqueous medium. Substitution of up to 15% of the water with *tert*-butyl alcohol increased the latex particle size and the molecular weight of the polymer. Pressures of 3000–5000 psig and temperatures in the range of 80–100°C. provided practical polymerization rates and stable latex products that could be concentrated by evaporation to 40–50% solids. The concentrated products were fluid and stable during storage for one year or more. Polymer isolated from the latexes exhibited a tensile strength of 1100–1400 psi, an elongation of 30–50%, and a Shore D hardness of 40–45.

#### INTRODUCTION

During the late 1930's in the laboratories of I. G. Farbenindustrie, Höpff, Goebel, and Rautenstrauch developed a process for the polymerization of ethylene in an emulsion system.<sup>1,2</sup> Patents based on this work disclosed that at pressures of 150 atm. or more and temperatures of 60–150°C., ethylene polymerizes readily in water containing anionic or nonionic emulsifiers and that persulfate and peroxides that induce free radical vinyl polymerization are suitable initiators. A more detailed report of Hopff's work appeared in 1946.<sup>3</sup>

Hopff worked with aqueous systems, not only to avoid the violent decompositions that sometimes occur in the bulk polymerization of ethylene, but also to circumvent the ethylene polymerization process patented by Imperial Chemical Industries. Very early, however, the German researchers realized that the emulsion-made polyethylene (which was cross-linked, insoluble, and softened at temperatures as high as 200°C.) differed greatly from that of the I.C.I. process. They attributed these differences to the large amount of initiator needed in their batch reactions. In the hope of producing better polymer by reducing the initiator requirements, they worked extensively with continuous systems. Yet they were able to make only a low molecular weight polymer that contained sulfate endgroups

and formed a water-sensitive film. The undesirable properties, particularly water sensitivity and insolubility, were attributed to the presence of the sulfate endgroups, because their removal by hydrolysis gave a soluble polymer that formed a clear melt. Although Hopff and his co-workers devoted considerable effort to characterizing the composition and structure of these emulsion polymers, especially those of low molecular weight, they reported very little about the mechanical properties of the polymer or about the properties of the emulsions. In addition to a few comments on the effect of temperature, pH, ratio of ethylene to water, initiator concentration, buffers, and some water-soluble solvents, they stated that emulsifiers did not decisively affect the reaction or the polymer properties.

Later work by other investigators is described in patents issued to du Pont, Olin Mathieson, Imperial Chemical Industries, Farbenfabriken Bayer, and Badische Anilin.<sup>4-14</sup> In some of the patent examples, the product is referred to as a "filterable dispersion," so it is doubtful that an emulsion polymerization even occurred. In general, the examples provide little information on the rates of polymerization and the effect of polymerization variables on properties of the polymer and emulsion. The use of *tert*-butyl alcohol in the emulsion polymerization recipe was shown to increase the molecular weight of the polymer, and in this respect it was unique when compared with other alcohols, acetone, and benzene.<sup>12</sup> A recent review by Sittig reflects the view held by many polymer chemists that the emulsion polymerization of ethylene goes with difficulty and gives emulsions that lack stability.<sup>15</sup>

Considerable research and development work has been carried out in the laboratories of the Spencer Chemical Division since 1958, and several Belgian patents relating to this work have been issued.<sup>16-19</sup> In this paper we describe the equipment and process suitable for the polymerization of ethylene in an emulsion system to a stable latex. Later papers will provide detailed information on the properties of the polymer and the emulsion—especially on the measurement of particle size—as well as on the rates and mechanism of the emulsion polymerization of ethylene.

## EXPERIMENTAL

### Apparatus

The polymerization vessel used for the majority of the work was a 1-gal. stainless steel autoclave equipped with a Magne-Dash agitator, a thermocouple well, a temperature indicator, external electric heaters which were controlled automatically, an internal cooling coil that was operated manually, and a pressure recorder. A dip tube and valve were provided for withdrawing samples during operation. A Hills-McCanna pump was connected to the autoclave for introducing an aqueous solution of initiator. Ethylene was supplied from a reservoir through manually-operated valves.

A portion of the investigation was conducted in an 18-gal. stainless steel autoclave equipped with a propellor-type agitator, thermocouple well, a

heating jacket through which a high-boiling organic liquid was circulated, an internal cooling coil, a pressure recorder-controller, and a temperature recorder-controller. A compressor supplied ethylene automatically as required to maintain the pressure. A sample line was provided for withdrawing samples from the bottom of the reactor.

### Raw Materials

The ethylene was a commercial grade suitable for polymerization. A typical analysis was as follows: ethylene, 99.68 mole-%; carbon dioxide, 0.156 mole-%; nitrogen, 0.009 mole-%; ethane, 0.132 mole-%; methane, 0.018 mole-%; oxygen, 0.001 mole-%. The water was either distilled or deionized. The *tert*-butyl alcohol was a pure grade obtained from Fisher Scientific Company. Inorganic peroxide, salts, and alkalis were reagent grade materials.

Fatty acids were USP products obtained from Mallinckrodt. Other emulsifiers were commercial products which were used as received.

### Procedure

**Anionic System.** The 1-gal. Magne-Dash autoclave was charged with a solution consisting of 1680 g. of deionized water, 200 g. of *tert*-butyl alcohol, 42.6 g. of myristic acid, 12.6 g. of potassium hydroxide, and 11.8 g. of tri-potassium phosphate ( $K_3PO_4 \cdot xH_2O$ ). The autoclave was sealed, then purged twice by evacuating and flushing with ethylene at 1000 psig pressure, and finally charged with ethylene to a pressure of 1500 psig. The agitator was started, and the charge was heated to 80°C. At this point, 120 ml. of a 4.8% solution of potassium persulfate was pumped in, and the pressure was increased to 3000 psig by addition of more ethylene. The polymerization started almost immediately, as indicated by a 300 psig pressure drop during the first 10 min. The pressure was restored to 3000 psig, and the reaction proceeded at a fairly steady rate. Each time the pressure dropped to 2700 psig, sufficient ethylene was added to raise the pressure to 3000 psig. The cumulative pressure drop provided a convenient guide to the rate and extent of the reaction. In addition, samples were withdrawn at intervals, and the solids content was determined by evaporating the sample on a moisture balance. The temperature was controlled at 80 $\pm$ 1°C. except for two short periods when it rose as high as 86 or 87°C.

The reaction, which had begun to slow down after about 1 hr. and had stopped after 4 hr., was terminated at 4 hr. and 10 min. The product, which had a pH of 9.0, was a bluish-white, fluid latex containing 24.4% solids. No floc was observed either on the walls of the vessel or suspended in the fluid.

The latex was stripped of *tert*-butyl alcohol and concentrated to 29.9% solids at reduced pressure in a rotating flask evaporator. The average particle diameter, established by a soap titration method which will be

discussed in a later paper, was  $0.038 \mu$ . The surface tension of the concentrated latex was 62.4 dynes/cm. measured with a DuNuoy tensiometer.

A portion of the latex was coagulated by addition to methanol containing a small amount of hydrochloric acid. The coagulum was washed thoroughly, first with methanol, then with water, and finally dried in a vacuum oven at  $60^{\circ}\text{C}$ . The resulting polymer had a density of 0.917 g./cc. and an inherent viscosity of 0.589 (determined on a 0.2% solution of the polymer in tetralin at  $135^{\circ}\text{C}$ .).

**Nonionic System.** An 18-gal. stainless steel reactor was charged with a solution of 64 lb. of distilled water, 12 lb. of *tert*-butyl alcohol, and 3 lb. of Triton N-101 (*p*-nonylphenol ethoxylated with approximately 10 molecules of ethylene oxide). The head space of the vessel was purged by evacuating and flushing twice with ethylene at 200 psig pressure. The agitator and heaters were turned on, and ethylene was pumped into the reactor to 2500 psig pressure while the charge was being heated to  $75^{\circ}\text{C}$ . A solution of 0.24 lb. of potassium persulfate in 4.0 lb. of water was added, and the temperature and pressure were adjusted to  $80^{\circ}\text{C}$ . and 3000 psig, respectively. After 1.5 hr. of operation, the temperature was increased to  $90^{\circ}\text{C}$ . and maintained at that point for the remainder of the run. The run was terminated after 3.5 hr.

The product, a white latex containing 18.8% solids and free of cream or sediment, was stripped of *tert*-butyl alcohol and concentrated to 40.2% solids by evaporation under vacuum in a rotating flask. The concentrated product had a pH of 7.5, a surface tension of 39.0 dynes/cm., and a Brookfield viscosity of 40.0 cpoise ( $25^{\circ}\text{C}$ ., spindle No. 1, 6 rpm.).

Polymer isolated from the latex by coagulating, washing, and drying had the following properties: inherent viscosity, 0.694; density, 0.9367 g./cc.; crystalline melting point,  $103^{\circ}\text{C}$ .; softening point,  $115^{\circ}\text{C}$ . (ring and ball method).

## DISCUSSION

The present investigation has included a detailed examination of many recipes and conditions suitable for emulsion polymerization of ethylene. It is beyond the scope of this paper to discuss the findings in depth, but we will set forth some influences which are of immediate interest.

Several types of anionic emulsifiers gave polymerization rates and latex stability that were completely adequate for all practical purposes, but others either prevented polymerization or produced an unstable latex. The potassium salts of lauric, myristic, and stearic acids were all quite satisfactory, but the potassium, ammonium, morpholinium, or triethanolamine salts of oleic acid behaved like an inhibitor. Sulfates of fatty alcohols such as sodium lauryl sulfate or sulfates of ethoxylated fatty alcohols such as the sodium salt of ethoxylated lauryl sulfate performed well with respect to rate and latex stability. Sodium sulfosuccinate esters were generally unsatisfactory because of the pasty condition of the latex at the termination of the run.

A variety of nonionic emulsifiers have been tested, mostly ethylene oxide adducts of various alcohols or phenols. Satisfactory polymerization rates and stable latexes were obtained with polyethoxylated octyl- or nonylphenols, but only if the adduct contained 9–15 units of ethylene oxide.

### Influence of *tert*-Butyl Alcohol

As shown by the data in Table I, the presence of *tert*-butyl alcohol significantly increased the particle size and molecular weight in both the anionic and nonionic emulsion systems.

In the nonionic system, an induction period of up to 2 hr. was reduced or eliminated by incorporating *tert*-butyl alcohol into the charge. Particle diameter had a rather erratic response, but with 15 or 30 parts of *tert*-butyl alcohol, the particle size distribution was considerably narrower than that observed with a low level or without *tert*-butyl alcohol. As the concentra-

TABLE I  
Influence of *tert*-Butyl Alcohol on Emulsion Polymerization of Ethylene

	Nonionic emulsifier				Anionic emulsifier	
	Run 426	Run 422	Run 277	Run 425	Run 388	Run 387
Recipe, parts						
Water	100	92.5	85	70	95	90
<i>tert</i> -Butyl alcohol	0	7.5	15	30	5	10
Triton N-101	3.0	3.0	3.0	3.0	—	—
Myristic acid	—	—	—	—	1.42	1.42
KOH	—	—	—	—	0.41	0.41
K <sub>2</sub> PO <sub>4</sub>	—	—	—	—	0.590	0.590
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.44 <sup>a</sup>	0.44 <sup>a</sup>	0.37 <sup>a</sup>	0.31 <sup>a</sup>	0.3	0.3
Conditions						
Temperature, °C.	80–90	80–104	80–100	80–90	78–89	80–93
Pressure, psig	3000	3000	3000	3000	3000	3000
Time, hr.	10.72	7.52	9.25	3.3	2.7	1.62
Latex properties						
Solids, % (unstripped)	9.4	17.0	17.2	17.2	24.4	26.4
pH	2.2	1.9	3.1	2.1	8.2	8.3
Appearance	White	White	White	White	Bluish	Bluish
Surface tension, dynes/cm.	30.3	29.7	—	—	70.6	68.4
Avg. particle diameter, μ	0.153 <sup>b</sup>	0.465 <sup>b</sup>	0.129 <sup>b</sup>	0.219 <sup>b</sup>	0.039 <sup>c</sup>	0.054 <sup>c</sup>
Std. deviation of particle diameter, μ	0.068	0.372	0.029	0.027	—	—
Polymer properties						
Inherent viscosity	0.225	0.440	0.878	0.850	0.486	0.655
Cryst. m.p., °C.	105–108	96–100	—	98–101	86–90	87–91

<sup>a</sup> Initial charge of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was 0.25 part. Increments of 0.06 part were added as required to sustain the reaction.

<sup>b</sup> Determined from electron micrographs.

<sup>c</sup> Determined by soap titration.

tion of *tert*-butyl alcohol was increased, inherent viscosity increased, and appeared to level off at a concentration of 15 parts.

Similar effects were noted in the anionic system. Increasing the *tert*-butyl alcohol level from 5 to 10 parts increased the average particle diameter from 0.039 to 0.054  $\mu$  and raised the inherent viscosity from 0.486 to 0.655. Although these are isolated runs, they are representative of effects which have been observed many times.

### Effect of Pressure

Early in our program we found that pressures of 3000–5000 psig afforded practical polymerization rates and yielded products possessing desirable latex and polymer properties. Hence the majority of our studies were conducted in this range. However, an attempt was made to evaluate the effect of pressure up to 20,000 psig. In one anionic emulsion polymerization at 20,000 psig, inherent viscosity of the polymer was 2.09, but instead of a latex, the product was a white powder. From another anionic run made at 15,000 psig, a latex was obtained containing polymer with an inherent viscosity of 1.211. The density of this material was 0.9173. A nonionic polymerization conducted at 15,000 psig produced a polymer with an inherent viscosity value of 1.10.

The experimental program was too limited and the results were too variable to determine quantitative relationships, but up to a pressure of 20,000 psig increasing the pressure did not result in a corresponding increase in polymer density and consequently was not a potential route to linear polyethylene.

### Effect of Temperature

Qualitatively,<sup>20</sup> the crystallinity of emulsion-made polyethylenes increases as the polymerization temperature decreases. We found that the rate of polymerization is increased as the temperature is increased, as one would expect. The latex stability was also influenced by the temperature, which is not surprising in view of the effect of temperature on the solubility of various components and on the rate of dissociation of initiator. Some typical results of polymerizations at various temperatures are presented in Table II.

### Latex Properties

The polyethylene latexes prepared under appropriate conditions were white, bluish-white, or translucent, and had low viscosity even at solids contents up to 50% or higher, that is, they resembled commercial latexes prepared from other monomers. According to measurements on electron micrographs the average particle diameter for the latexes investigated fell between 0.03 and 0.15 $\mu$ . The latexes prepared with fatty acid emulsifiers were generally unsaturated, i.e., they contained less soap than the amount required to saturate the surface of the polymer particles. The

surface tension of such latexes, after removal of any *tert*-butyl alcohol present usually fell between 35 and 70 dynes/cm. In order to prevent the development of "cream" in latexes prepared with nonionic emulsifiers it was found necessary to terminate the reaction at a solids level below the point where the particles became unsaturated. Consequently, the surface tension values of the nonionic latexes were kept between 28 and 35 dynes/cm.

The stability of the latex to mechanical action was tested by agitating it for 60 sec. in a Waring Blendor. The mechanical stability of an anionic latex was low when the surface tension of the latex was high. However, by

TABLE II  
Effect of Temperature on Emulsion Polymerization of Ethylene

	Run 587	Run 576	Run 489	Run 644
Recipe, parts				
Lauric acid	1.23	1.23	1.23	—
Triton N-101	—	—	—	3.0
<i>tert</i> -Butyl alcohol	20	20	20	15
KOH	0.41	0.41	0.41	—
$K_2PO_4 \cdot xH_2O$	—	—	0.5	—
$K_2S_2O_8$	1.5	0.25	0.305*	0.25
$NaHSO_3$	0.1	0.10	—	—
$FeSO_4 \cdot 7H_2O$	0.42	0.07	—	—
$Na_4P_2O_7$	0.66	0.11	—	—
Conditions				
Temperature, °C.	22	50	110	121
Pressure, psig	4500	4500	4500	4500
Reaction time, hr.	9.9	19.5	3.4	5.5
Latex properties				
Latex solids, %	8.6	10.2	19.2	13.8
Latex appearance	White fluid	White viscous	White fluid	White chalky

\* Initial charge was 0.185 part. Two increments of 0.06 part each were added to sustain the reaction.

addition of more surfactant of either the same type used in the polymerization or another type, its stability could be improved so that it would not thicken or coagulate during the test. Those nonionic latexes that were fluid and stable when they came from the polymerization operation invariably exhibited good mechanical stability if the surface tension was less than 35 dynes/cm.

The anionic emulsions differed in stability to storage over a long period depending on surface tension, particle size and type of emulsifier. Generally, the latexes were stable and did not coagulate or gel during storage, but some latexes developed on their surface pieces of flaky material. Others formed a "collar" or a layer of "cream" as a result of large particles rising to the top. The large particles may have been present originally or they may have formed by agglomeration during storage.

Among the nonionic latexes, shelf stability was excellent provided one observed the previously mentioned requirement of keeping the solids level during polymerization low enough so that the particles did not become unsaturated. This condition was obtainable at practical solids levels with the ethoxylated alkyl phenols containing 9–15 ethylene oxide units and with some other types of nonionic emulsifiers. When this requirement was not met, various degrees of instability were observed from collaring to complete separation of solids.

As has been noted so often in the past in other latex systems, the development of a stable latex is largely a question of trial and error and of matching the properties of the surfactant with the properties of the monomer and with conditions that prevail during the polymerization operation.

None of the latexes described here was freeze-thaw stable. The nonionic latexes were stable to the addition of acids, bases, and multivalent cations, whereas the products stabilized with fatty acids were readily coagulated by the addition of acids or multivalent cations.

When cast on glass and evaporated at room temperature or at 100°C., the latexes dried to films that were fragmented or interlaced with cracks rather than continuous. The films were not redispersible in water. Presumably the polymer contained in the latex was too hard to enable the particles to deform and fuse together sufficiently during the drying operation to form continuous films at elevated temperatures. On other substrates, such as paper, particularly in thin coatings (0.001 in. or less), dried at 100°C. and kept hot several minutes after drying, coatings were obtained that were impervious to water and exhibited low moisture vapor transmission rates comparable with those of extruded polyethylene films of the same thickness and density.

### Polymer Properties

Polymers isolated from the latex by coagulating with acid and methanol or acetone followed by washing with water and methanol and drying in a vacuum oven, were compression-molded into test strips, and their physical properties were studied. The results varied with the recipes and polymerization conditions, but for polymers prepared between 3000 and 5000 psig and at temperatures of 80–100°C., the properties were in the following ranges: tensile strength, 1100–1400 psi; elongation, 30–50%; Shore D hardness, 40–45.

### References

1. Hopff, H., and S. Goebel (General Aniline and Film), U. S. Pat. 2,334,195 (Nov. 16, 1943).
2. Hopff, H., S. Goebel, and C. W. Rautenstrauch (General Aniline and Film), U. S. Pat. 2,342,400 (Feb. 22, 1944); H. Hopff et al. I. G. Farbenindustrie, Ger. Pat. 737,960 (July 1, 1943).
3. Hopff, H., and R. Kern (transl. by G. M. Kline), *Modern Plastics*, **23**, No. 10, 155 (1946).



4. Brooks, R. E., M. D. Peterson, and A. G. Weber (du Pont), U. S. Pat. 2,388,225 (October 30, 1945).
5. Harmon, J. (du Pont), U. S. Pat. 2,462,390 (Feb. 22, 1949).
6. Seed, L. (ICI), U. S. Pat. 2,542,783 (Feb. 20, 1951).
7. Berry, K. L. (du Pont), U. S. Pat. 2,559,752 (July 10, 1951).
8. Seed, L. (ICI), U. S. Pat. 2,592,526 (April 15, 1952).
9. Becker, W., and O. Bayer (Farbenfabriken Bayer), U. S. Pat. 2,695,899 (Nov. 30, 1954).
10. O'Flynn, D. J., and D. G. Pye (du Pont), U. S. Pat. 2,739,058 (March 20, 1956).
11. Olin Mathieson, Brit. Pat. 715,875 (Sept. 22, 1954).
12. du Pont, Brit. Pat. 721,678 (Jan. 12, 1955).
13. BASF, Brit. Pat. 798,565 (July 23, 1958).
14. BASF, Brit. Pat. 813,814 (May 5, 1959).
15. Sittig, M., *Petrol. Refiner*, **39**, 162 (1960).
16. Spencer Chemical International, Belg. Pat. 611,101 (Dec. 30, 1961).
17. Spencer Chemical International, Belg. Pat. 611,102 (Dec. 30, 1961).
18. Spencer Chemical International, Belg. Pat. 616,650 (Oct. 19, 1962).
19. Spencer Chemical International, Belg. Pat. 621,386 (Feb. 14, 1963).
20. Helin, A. F., H. K. Stryker, and G. J. Mantell, *Soap Chem. Specialties*, **38**, No. 3, 85 (1962).

### Résumé

On décrit les formules et les conditions opératoires de la polymérisation en émulsion de l'éthylène. On a obtenu des produits stables de consistance élastique avec plusieurs émulsifiants anioniques et non-anioniques, mais, dans la majorité des cas, on a utilisé des acides gras ou des polyalcoylphénols éthoxylés. Le persulfate de potassium est un initiateur satisfaisant à des concentrations de 0.05 à 0.50 part par 100 parts du milieu aqueux. Si l'on substitue jusqu'à 15% de l'eau par de l'alcool *t*-butylique, on augmente la dimension des particules du latex et le poids moléculaire du polymère. Des pressions de 3000 à 5000 livres par pouce carré et des températures de l'ordre de 80 à 100°C engendrent des vitesses de polymérisation satisfaisantes et des produits élastiques stables, qui peuvent être concentrés par évaporation jusqu'à 40 à 50% de matière solide. Les produits concentrés ont une consistance fluide et sont restés stables lors d'une conservation d'une année et plus. La polymère isolé des particules de latex a présenté une résistance à la tension de 1100 et 1400 livres par pouce carré, une elongation de 30 à 50% et une dureté 'Shore' 'D' de 40 à 45.

### Zusammenfassung

Rezepte und Arbeitsbedingungen für die Emulsionspolymerisation von Äthylen werden beschrieben. Mit verschiedenen anionischen und nichtionischen Emulgatoren wurden stabile Latizes erhalten; für den grössten Teil der Arbeit wurden jedoch Fettsäuren oder polyäthoxylierte Alkylphenole verwendet. Kaliumpersulfat funktionierte bei Konzentrationen von 0,05 bis 0,50 Teile pro 100 Teile wässriges Medium zufriedenstellend als Starter. Ersatz von bis zu 15% des Wassers durch *t*-Butylalkohol führte zu einer Erhöhung der Latexteilchengrösse und des Molekulargewichts des Polymeren. Drucke von 3000–5000 lb/in<sup>2</sup> und Temperaturen im Bereich von 80–100°C führten zu einer praktisch brauchbaren Polymerisationsgeschwindigkeit und zu stabilen Latizes, die durch Eindampfen zu einem Festkörpergehalt von 40–50% konzentriert werden konnten. Die konzentrierten Produkte blieben während der Lagerung durch ein Jahr oder länger flüssig und beständig. Das aus den Latizes isolierte Polymere besass eine Zugfestigkeit von 1100–1400 lb/in<sup>2</sup>, eine Dehnung von 30–50% und eine Shore-“D”-Härte von 40–45.

Received September 28, 1964