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POLYSTYRENE FOR EVERY NATION[1]

by

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Friends, we are gathered here today to answer the call of the United Nations to extend a helping hand to all our neighbors, the nations of the world.

Some of us are more adequately endowed with money, materials and know how than others. Along with these gifts, comes a responsibility of generosity. Each of us could do better, all of us can become great. In every one of us is the desire to succeed. Today, we will endeavor to enkindle a technical spark and to light up the fire of renewed faith in ourselves by our disclosures to each other during this meeting.

We are going to talk about the practical methods of polymerization of styrene which have been used over the past 30 years. First, a brief history of some of these processes, their advantages and disadvantages, how they work and the types of materials that they produce. Then we will review in some detail, low cost methods for making polystyrene that are simple, sound, and require little sophistication on the part of the operators and the technical manpower running these plants. The more practical of these methods and some direct economic comparison of plants to produce polystyrene will follow. Finally, we will present easy mounted, low cost polystyrene plants for your consideration and make recommendations so that technically oriented people of your countries will be able to make a decision.

Historical

The commercial age of polystyrene is about 30 years but history has recorded that a gum called Storax came from certain trees. Bostare and Simmers (1931) describe experiments in which styrene monomer was changed into higher order material "Styrol Oxide". Hoffman and Blyth, heated styrene in sealed tubes at 200°C and obtained solid products in 1845. In 1911, Matthews filed a British patent 16,277 which described a thermal and catalytic process for polymerization of styrene monomer to yield a substance for the production of articles formerly made from celluloid glass, hard rubber, and wood.

Many of these early polymers were low grade and suffered from impurity of the monomer and it was not until Moureau and Defraisse (1922) found that the aromatic amines and phenols inhibited the polymerization of styrene, that efficient distillation and improved storage opened up the styrene market.

Ostromislensky, in a Russian Physical Society Journal and later in some patents to Naugatuck Chemical Company, showed that various materials were obtained from different polymerization processes and that lower temperatures, produced better resins. Ostromislensky also in the late 20s, used the peroxides for this polymerization work.

The polystyrene materials in the 20s and the 30s had a tendency to craze and crack after a week or two of commercial use and mechanically they were inferior.

By 1937 in the U. S. Dow, followed by Monsanto and Bakelite, started to supply polystyrene to the plastic trade but in 1938 there were only 200,000 pounds of polystyrene. Also, in Germany, during the mid 30s, six or seven varieties of material called Trolitul were being offered to the trade and these were varieties of molecular weight and in some instances, copolymers with acrylates. Historical highlights are given in Figure I.

The second world war put a great emphasis on the U.S.A. on styrene for synthetic rubber. At the end of the war, tremendous amounts of styrene monomer were available. Many research departments were doing work with styrene through the late 30s and early 40s. Whereas 1938 produced only 200 thousand pounds, by the end of world war two, it was estimated that there was close to 50 million pounds, an increase of 250 times. By 1961, this reached 11 thousand million pounds, and by 1966, the production of polystyrene and its many varieties reached 2 thousand million pounds. It is predicted that the 3 thousand million pound market in the United States will be reached by 1969. A quick review is given in Figure II of U.S.A. production.

Polymerization techniques

Most of the early works of Ostromislensky, Lemoine and Konstein were done with mass polymerization techniques, primarily by heat alone.

With the discovery that peroxides could also initiate radical polymerization, the field opened up considerably in the formation of polystyrene. In the mid 30s, a tremendous amount of work was started in many of the nations on emulsion polymerisation, using a variety of techniques which allowed one to make synthetic rubber which by 1938 was approaching the best natural material in properties and wear. It was inevitable with this tremendous push brought on by world war II, that other techniques for the polymerization of polymers and especially polystyrene would be developed.

As the size of the mass reactions grew, it was obvious to almost everyone that it was impractical to produce large amounts of polystyrene in any single unit. The first U.S. commercial application was the so called Can process of Dow Chemical Company where the polymerization was carried out in a series of baths increasing in temperature between about 70° to 170°C. Cans were successively moved to a higher and higher temperature and after the polymerization was complete, the tin was stripped from the polystyrene block and this was crushed, devolatilized by being heated and passed under a vacuum to remove the residual low volatile materials.

In the late 30s and the early 40s, the Germans practiced a polymerization technique which advanced the polymerization in rather large stirred vessels to approximately 35% polymer and then the materials were run down through towers which had heating and tremendous cooling capacities built in to them and the very viscous liquid materials were run off into a movable belt which passed them under heat and vacuum to remove the volatiles of this product line. Each of the two mentioned processes obviously felt that the greatest deterrent to the polymerization was the removal of heat from the mass product. Since the emulsion polymerization techniques did not suffer from this particular difficulty, because of the water available to remove excess heat, immediately attempts were made to polymerize styrene in workable formulations by modification of the rubber techniques that were then available. However polystyrene made in this way, was of very high molecular weight and did not prove to be usable in the machines and the applications that were then being tried out for the infant polystyrene business.

Persistence however, along these lines finally developed suspension polymerization and one of the early publications of this work is (Hohenstein) in Indian Rubber World where by using finely divided tricalcium phosphate, he was able to produce a bead or sugar polymer which had excellent molding characteristics. In suspension, the prime problems that exist in mass polymerization, that of removal of heat, was not encountered. When the suspension system was also coupled with the use of a peroxide, the polymerization could be run below the boiling point of water and this made for much easier operation than had been the practice in the mass polymerization technique, which used cans or a continuous tower in combination with kettles for polymerization.

An early mass polymerization technique passed the prepolymerized polymer into a tray or press where the platens served to cool the reactants. As long as a large area per unit volume was built into these press processes, some fair control was experienced. However, the press reactors as they were run through the early 40s and 50s, left much to be desired from a safety viewpoint and also from the preparation of the best types of materials, because of local overheating.

As techniques improved, the mass polymerization and the suspension polymerization proved to be the most economically attractive methods of preparing good polystyrenes. Along with the improvements in the polymerization system, also came improvements in the feed mechanisms and the ability to degas or devolatilize many materials which were high in volatility. The advent of the vented extruder helped a lot in this area.

Along with the development of the techniques of polymerization for polystyrene which gave good and acceptable commercial types of material, also came many advances in the understanding of the actual mechanism of the reactions and what one must do in the polymerization in reference to time, temperature and other variables to make the most acceptable products.

A great deal of time and effort through the 40s and early 50s went into the study of the physical properties of the polymers and the various techniques for the manufacturing of these polymers. It was early evident that the crystal material, because of its shattering nature, had to be improved in impact qualities and many attempts at polymerization of styrene with rubber and of mixing styrene with various rubbery materials were made.

Types of Materials

As the sophistication of the end user developed and the knowledge acquired by the material manufacturers became clear, it was obvious that no one type of material would fill the needs of all of the polystyrene uses of the early 50s. It was also apparent that the crystal clear nature of polystyrene was an immediate advantage but that the shattering or brittleness of the material was one of its major disadvantages.

Immediately blends of polystyrene and rubber began to appear on the market in the late 40s and early 50s and although these materials left much to be desired in the actual blending, they were immediately accepted by the trade as impact materials and as their use grew, so did the knowledge of polyblending techniques. It was not long before it was immediately obvious that if a person wanted to mix materials to the best advantage, he should somehow mix them at a point where their viscosity were somewhat equal. This immediately started people running viscosities on polystyrenes and rubbers and trying all combinations of the particular methods of operation. Eventually, it proved that if a mix was run on a two roll mill, somewhere around 160°C with a Goodyear type 1006 and an easy flow type of polystyrene, that a fairly good and controlled blend could be made which had the best possible physical properties. It was not long after this that the technique of master batching were 50% rubber and 50% polystyrene were prepared on a two roll mill and then this was let down from five to one to nine to one with more easy flow polystyrene crystal to manufacture the better grades of impact polyblend polystyrene that were in the market in the early 50s.

At the same time, this blending technique was being developed, work was going on in the study of the polymerization of styrene monomer in the presence of various rubbers.

Properties

It is extremely important that one understands the physical properties of polystyrene and how they relate to the molecular weight. As the molecular weight of polystyrene increases, it turns slowly from a liquid to a semi-solid and finally to a solid. On the basis of the molecular weight of styrene being 104, one thousand units of styrene would have a molecular weight of 104,000. It also happens that a molecular weight of 104,000 is a very excellent tensile strength polymer. Molecular weights much above 100,000 are increasingly more difficult to mold while molecular weights from 104,000 down to about 70,000 are increasingly less difficult to mold. However, as the molecular weight drops below 70,000 the physical properties such as the tensile strength, the impact strength, the compression strength and elongation, tend to fall off quite rapidly. A typical property versus molecular weight diagram would look something like Figure III.

One property does not seem to depend upon molecular weight as much as it depends upon monomer or volatile content, i.e. the total amount of polymerization. In Figure IV, this property called heat distortion is shown to be directly related to the amount of free monomer and/or volatiles such as ethyl benzene in the finished product. This plots the effect of heat distortion versus volatile content and it is pretty obvious that approximately a 2/10 percent increase in volatility has an effect of dropping the heat distortion temperature of materials about 1°C. In early manufactured polystyrene, probably the single most important, detrimental, and negative factor was the amount of free monomer left in the polymers that were made. This was partially due to the fact that the styrene monomer was not of sufficient high purity to make the best type of polystyrene. Quite rapidly from the 30s up through the 50s and 60s, heat distortion temperatures rose from about 63°C on a molded piece to approximately 93-94°C on today's materials. The best heat distortion materials can go up to 96-98°C. This was primarily due to the reduction in volatile content by two factors, one a better styrene monomer and second, better polymerization techniques, that more completely polymerized the monomer. It is undoubtedly true that the mass techniques with their higher temperature are more susceptible to monomer content and volatility than the materials prepared in the suspension polymerization. Suspension polymers are more completely polymerized and they do not have to go through the devolatilizing process. It is also true that the purer the monomer, the less likely the impure ethyl benzene is likely to act as a chain terminator reducing [illegible] weights.

Between the 75,000 and 100,000 molecular weights polymer, there are a number of [illegible] consistencies will be suited for the different end uses. The higher molecular weight material will have slightly better strength but will be [illegible] to mold than the lower molecular weights. [illegible] application which needs high strength would be ideally suited for [illegible] of polymer. This is usually referred to as high [illegible]. The middle of the molecular weight range, would be known as [illegible] polystyrene and it would generally be quite easy to mold and would have an intermediate strength. As long as the volatility was kept at a fairly low level, somewhere around 2/10 of a percent it would be a general purpose type of material. However, in the medium [illegible] (.01% and below), it would be very difficult to put [illegible] material into the [illegible] the production requires [illegible] flow [illegible], which usually have molecular [illegible] 70,000 [illegible] but more [illegible] particular [illegible] purpose and the high strength [illegible] particularly [illegible] less viscous and [illegible] satisfactorily [illegible] in the process. [illegible] six seconds are [illegible] with this type of material [illegible].

By using two [illegible] polymerization cycles [illegible] heat distortion materials can be made of [illegible] purpose or high strength material which are suitable for [illegible] operation and bi axially oriented sheets. In general, the two [illegible] are active at different temperatures and it only remains [illegible] tion process [illegible] temperature to activate the [illegible] monomer content of the high heat distortion type material to a minimum. Heat distortion materials as low as .05% of monomer are reported in the literature.

Besides the molecular weight which are usually measured by a viscosity of a certain percentage of polymer in toluene by either a viscometer tube or a Brookfield viscometer, the distribution of the molecular weight is also quite important. In Figure V, the best types of materials for the three types mentioned above, shows a simple hyperbolic curve, very similar to the quality control chart of populations. There will be about an equal tail of low molecular weight and high molecular weight material but the major portion of distribution is in the middle and concentrated with peaks at the 70,000, [illegible],000 and 100,000 molecular weight. The addition of plasticizer shifts the molecular weight average, however, plasticizer is not usually used in enough concentration to make a second hump in the molecular weight distribution. The plasticizer usually used is white oils of medium viscosity, however quite a few people have used a polystyrene known as PS-2 which has about [illegible],000 to [illegible],000 molecular weight, which are added to polystyrene in amounts up to 3-4% maximum.

From the foregoing, it is understandable that the molecular weight and the manufacture of the polystyrene must be well controlled by the use of the free radicals that are made during the polymerization process. Since free radical manufacture is somewhat dependent upon the half life of the catalyst and the temperature, if the catalyst amount is made to increase, the molecular weight will drop, because there will be more free radicals in competition for the amount of monomer in a given time and temperature than there is with less catalyst or at a lower temperature. The molecular weight is inversely proportional to the square root of the catalyst concentration but practical changes of adding more or less catalyst and raising or lowering temperature, control the molecular weight prepared. It does remain however for the control chemist, to make sure that the viscosity of materials fall within limits for adequate molecular weight control and also to make sure that the volatility fall within similar limits for each type of material to make sure that the heat distortion and the completeness of polymerization are satisfactory in the industrial end use.

Impact types

Using techniques based on crystal polymerization some improvement in the impact strength was obtained by blending rubbers. It did not complicate the engineering and the chemistry too much and it was quite easy to produce such polystyrene using either polymerization techniques by the mid 50's. Research to produce higher impact polystyrene by suspension polymerization of a rubber-styrene solution was a more difficult problem and required approximately five years of concentrated effort of many people to make suspension impact polymers. It seemed that once Stein and Waters of Monsanto had their patent issued, then almost immediately a great many numbers of people were able to completely polymerize in stable suspension systems, rubber mixtures with as much as 5-7% rubber. It was much more difficult to make the 15-20% rubbers. But with today's polymerization stabilizers in the suspension system, even this is possible.

At the same time, the polymerization techniques were being improved, the rubbers also improved and the early used 1006 hot rubbers gave way in rapid succession to the Krylene NS and some of the cold rubbers, followed by an S630 and eventually the butadiene type, which are now almost exclusively used in the United States. The butadiene type of rubbers give a much better impact at low temperatures and are more effective in producing impact than the previously used rubbers. About 60% of a butadiene rubber will give the same impact (foot pound per inch of notch) as the previous 1006 or Krylene NS.

In general, the types of impact polystyrene that are on the market are a medium impact of about 0.5 foot pounds, the 1.2 to 1.5 impact, which is the general purpose impact in today's market and a high heat distortion material which is recommended for appliances that require heat balance, and heat resistance. Using the techniques that have previously been described in crystal type, molecular weight changes can be affected to make a material easier or harder flow, more or less plasticizers can be added however, it is generally felt that for extrusion materials, plasticizers should be kept to a minimum below ½%. Injection molding materials can stand substantially more, as much as 2½% of plasticizer.

With rubber in polystyrene containing the butadiene unsaturated bond, it was important that both heat stabilizer and antioxidants were added into the impact polystyrene almost from the very beginning of the polymerization to protect the rubber so it would not be degraded. It was also extremely important in the working of any impact material that the temperature should not exceed about 220°C in processing, so that the rubber would not be killed. With the protectants available, effective use of impact materials was possible.

More recently materials known as the third generation polystyrenes (impact materials) have been developed where heat distortions have been raised to 105° to 108°C and where impacts are possible between 4 and 5 foot pounds. A good deal of this is processing techniques along with catalysts and programming of temperature, with possibly the use of some cross linking agent in very small amounts and the reduction of volatile matter to a minimum.

The possibility of making ABS types of materials by impact polystyrene know how is very important. It probably is true that the lower grades of ABS, possibly up to the eight to ten foot pound level, can readily be manufactured by impact polystyrene know how which avoids the basic emulsion systems of the early ABS's. A number of people in the United States are manufacturing by this technique. More recently blends of SAN and especially prepared emulsion high butadiene content rubber make even the higher ft./lb. ABS's possible.

The patent situation

The patent situation must be answered by the patents in effect in each individual country. In the United States, a number of Court actions have indicated that the use of TCP in suspension polymerization as practiced in the United States seems to be relatively open art. In a recent suit of Koppers against Foster Grant, the Court has declared Koppers' patents invalid and the appeal has been rejected.

There is one patent to Amos, McCurdy and McIntyre of Dow, U.S. 2,694,692 which seems to cause some concern in the impact polystyrene field. This patent claims the use of shearing in the prepolymerization system in order to make a good impact polystyrene. The teaching of this patent is correct and the best impact is made with early agitation in the prepolymerization kettle. This patent, issued in 1954, is therefore in force until 1971, according to the seventeen year law of the United States. What will be decided in this case in Court is conjecture. I am merely calling it to the attention of the people who read this article.

In the field of ABS, the fact that Union Carbide and Marbon were in interference has caused the patent to Union Carbide to be issued in 1965 and the patent to Marbon to be issued in 1966 and because of this, the ABS patents have to run until 1982 and 1983. These patents issued earlier in some other countries. With this ABS technology pretty well patented by Union Carbide and Marbon, it is not surprising to find the impact technique method of making ABS attractive and being pursued by the raw materials people in the States.

How each countries patents are issued could not be discussed here but at least these major highlights should be mentioned.

Description of process

A brief description of the mass process for polymerization of impact material follows: rubber is cut and dissolved in styrene and after passing through a filter to remove gels and unwanted emulsion aids, the polymerisation is started in a stirred autoclave until the polymer content reaches approximately 35-40% solids. This can be done either thermally or with the help of catalyst, either benzoyl peroxide or azobisisobutylnitrile or similar materials. After about 40% solids the material is placed into a press or run into a continuous tower where further polymerization takes place. In the press, it is run at about 90°C then raised to 125°C and then to 100°C to complete the polymerization is approximately 12 to 14 hours. In a continuous tower the material passes down through zones, usually four set at 90°, 130°, 150° and possibly 200°C. In the so called press block method, the material is removed from the press, ground, and extruded and the volatile content reduced by a vented extruder. In the continuous process, the material is devolatilized over a thin film evaporator or a herringbone gear devolatilizer and the volatile material recycled to the process. After the devolatilization is complete, gear type pump can pump the materials through a spinnerette and the final pellet made. However, quite often the operation uses an extruder instead of a gear type pump and goes through the exact same process that the block polymerization materials go through.

In a suspension process, for impact, Figure VI the operations are similar until the 40% polymer is made and then the material is suspended into a water TCP prepared kettle in about 50-50 proportions and with a series of temperature rises, from 90° to 115° to 130° in a period of 8 to 10 hours, the polymerization is completed and usually this is in the presence of two catalysts, such as benzoyl peroxide and ditertiary butylperbenzoate. The material then is flushed out of the reactor onto a mechanical separator which separates the 400 mesh TCP from approximately the 80 mesh impact beads. Materials are then washed through a centrifuge, dewatered and passed through a drier where the volatile content is reduced to approximately .5 to .7%. The materials then go through a devolatilization extruder to reduce the content to approximately the .2 to .2% volatiles or lower if heat resistant material is desired.

In the manufacture of crystal (Figure VII) the impact prepolymerisation stage is not used and the monomer is pumped directly into hot water which contains the TCP and dyes, plasticizers and catalysts are added directly to the polystyrene and then the conditions for making the beads are a certain temperature, certain fullness of the kettles, certain rpm's of the stirrer and with experience, very accurate control of the proportion of beads that you can put on 40 to 60 mesh is accomplished. After the crystal comes out of the kettle, it too is washed mechanically or the TCP is separated by HCI acid with less than 10 parts per million of iron, and it passes through the centrifuge and is dried. However, drying of crystal is much more readily accomplished than impact polystyrene. The rubber seems to hold a lot more water and it is about five to seven times as hard to dry as crystal polystyrene.

Advantages and disadvantages of methods

In general, there are certain advantages and disadvantages in each of these processes. The press and the mass continuous process do not polymerize as fully as the suspension process and the temperature that is used in the polymerization is usually quite a bit higher by as much as 75° to 100°C. This makes it more difficult to completely polymerize since the reverse reaction of depolymerization starts taking place and this requires therefore the addition of devolatilization in the actual process for the manufacture of a suitable polystyrene. However, the manpower requirements of a continuous operations are lower. The press process manpower requirements are high and in countries where economy of manpower is important, such as the United States, it is not a good method. However, where labor is cheaper, the press process has proved very satisfactory. The unloading of the press and the grinding have been made automatic in some instances and this is practiced in Great Britain and in Russia. The big advantage of the continuous process is that usually you can avoid the use of chemicals such as peroxides and suspending agents and therefore inherently can have a lower materials cost than the suspension process.

The suspension process undoubtedly has the better heat history for the polymer in that it has a lower heat exposure than in the continuous and press process and there is much better heat control in that the water is able to keep the process temperatures almost exactly as set with no override. However, water goes along for the ride and besides heating it up, it has to be removed and this costs money. However, in a country where overnight delivery is expected, the suspension process is ideally suited because one grade of material can follow another rapidly without any cross contamination and a batch of easy flow could follow a batch of high heat distortion materials, whereas in any continuous process, there has to be enough time for a changeover and sometimes this is as much as 24 to 48 hours. In this regard, the suspension process can reduce storage facilities, hold up and delivery and it is often said in the United States that it would be better to establish four, forty or fifty million pound plants at areas of concentration of end use, rather than a 200 million pound plant in any one location. It is felt that a cost of shipping of over 75 cents in the United States would be more than any saving that can be shown in any process operation of a large scale type in any one location.

Although there are many facets to the polymerization techniques none of them are so complicated that it would not be easily understood by any country in the world where a chemistry or chemical engineering course is taught in the schools. In reference to the suspension process, it only remains that a good water of sufficient quality and quantity be found to allow the suspension polymerization. With today's ion exchange system, it is possible that any water can be made suitable for a suspension system. However, this does involve some cost. Initial cost of equipment and the regeneration costs (acid and caustic) will increase with the amount of ions to be removed. In the mass polymerization areas, water is no problem, but the ability to control the polymerization temperature is. This control of reaction temperature was and is a problem and although no danger to safety has arisen in the United States from this practice, I am sure that great variations in end product have resulted from uncontrolled reactions in the polymerization zones.

In the United States, the early plants (Dow and Union Carbide) were the tower process. The economics were completely different than they are today and there are many large tower processes in operation with very high output and these were somewhat like Topsy, they just grow. It would be a little surprising today if anyone entered into the field of polymerization with units copied on the large scale continuous polymerization systems. Each year however, more effort is being put into small scale polymerization techniques and know how on mass and these particular efforts are starting to bear fruit.

Newer processes

Typical of one of these operations is a Process C, developed by the Polymer Corporation of Canada and this is ideally suited for someone who can use from seven to fifteen million pounds of a particular type of polymer. Recently on two week length runs, on various grades by Process C has proved satisfactory. All grades of crystal and impact have been made by this process. Some further effort on highest heat distortion materials and low melt index materials is needed. This Process C also can be used for polymerization of other monomers and copolymers. Its best features are uniformity of product and clarity of crystal. Some production of both grades crystal and impact on a single unit has been done. These units are ideally suited for complete integration in processing operations, e.g. someone let's say manufacturing a biaxially oriented material or a formable egg carton or other suitable large outlets where processing by extrusion and forming or blowing is part of the operational techniques. Certainly an operation of this kind where a continuous polymerizer feeds monomer into one end of a plant and the finished product is shipped out the other end, in almost 100% yields, make for ideal economics. The heating and the re-extruding of the polymer would be eliminated and with the proper choice of integrated units, matched to the outlet delivery of the polymerization section, multi lines could be run off, producing a variety of finished products. Actually, one could visualize a multi unit, small scale polymerization set up using four walls of a square building units, making closures on one wall, colored materials for sale on another wall, pipe on a third wall and crystal for sale on a fourth wall. This set up may be the future plant and not too far in the future, if the polymerization techniques continue to grow as rapidly in the next five years as it has in the past.

Economics

The decision on what to do, when to do it, and how to do it, are not a matter of preference, they are basically a matter of economics. A polymerization plant to manufacture polystyrene is expected to be competitive for seven to ten years and meet any competition on prices and quality. At the same time, it must make a profit and return interest on the investment while it supports research and technical service to the customer. In the United States, this is of concern, however with the firming of prices and some rising prices in the polystyrene field the industry is in a good and healthy condition and all of these economic conditions are being met. However, in each of your countries, economic conditions are somewhat different but assuming that a packaged plant can be purchased and erected, with a minimum of engineering know how required on the part of the company purchasing it, it would appear that the best way to approach this particular subject in which we are all deeply involved, is by a calculated plant, capable of making forty million pounds of polystyrene of various types by the two best low cost processes available in the industry today. In my opinion, the Process C operation of the Polymer Corporation for underdeveloped countries or for integrated plants, is without parallel and in a relative class by itself by as much as 1/2 cents a pound over the next cheapest quick response, variable type operation that could be accomplished by a suspension polymerization plant.

A typical suspension floor layout is shown in Figures VIII and IX. A plant using this arrangement can be operated at an annual production of 40-50 million pounds per year of impact, various types, and crystal, various types. Some segregation must be maintained as shown in the layout so that contamination will be impossible between impact and crystal materials.

A typical layout on Process C is indicated in Figure X. Here a multi unit of 5 reactors would allow one to manufacture 5 different types of material continuously without contamination. Storage must be segregated especially since impact easily contaminates crystal. The Process C units have integrated devolatalisers pumping out the reactors and at the same time, extrude, devolatilize and can color the output from each reactor.

The output of the suspension plant is in the form of beads (sugar) and in countries where screw injection machines are prevalent, can be directly used. In ram type injection molding equipment, the beads gall the ram and seriously damage the cylinder and the beads must be extruded into pellets (colored at the same time) for this injection machines.

Over the past year, considerable time and effort was spent in making direct comparisons on the capital cost of two plants, to manufacture the various grades of polystyrene by these two processes. By the way of quick review, submitted for your consideration is the economic comparisons on as close and similar basis as possible of Process C and suspension polymerization. Due to the nature of Process C, with its non use of catalyst, or at least very light use of catalyst, and its very accurate control of polymerization techniques, and its ingenious unit design and its process control features and its very excellent use of an extruder as a pump to do the final devolatilization and coloring and by the very fact that it is continuous and in multi tower systems which could be run efficiently by a minimum of manpower, there is certainly a saving of about ½ cents to possibly a saving of as much as .75 cents a pound in the forty million pound plant. Direct costs are compared in Tables Crystal Figure [illegible] and Impact Figure XII.

In Process C, the highest heat distortion materials and the lowest melt index materials are not known as yet. Heat distortions of [illegible].5 and melt index of 5-6 are currently being made. Probably techniques of polymerization will readily raise these properties in Process C. Whether Process C can match the suspension polymerization with its very high heat distortion and the very accurate control and low heat history, remains for the future. Polymerization in the suspension area can be increased with a more rapid through put per dollar invested than is currently being practiced. Process C is newer and has less production history than suspension but has great promise in integrated lines and smaller output operations, but with experience, output should improve and the highest quality materials should result.

From the comparisons above, it surely seems obvious that in those countries where water can be a difficulty that Process C would be the most likely approach to polymerization of styrene. However, where water is not a problem suspension polymerization should be considered and although it may cost slightly more with today's economics, it may be possible in the future to change the batch operation to a continuous operation but it currently has not been done with any degree of success as of the moment.

Conclusions

This paper would be certainly incomplete if some suggestions were not made to each of you on how you might approach the problem and decide for yourself how best you can operate in your own individual country. First, it is important to find out what the going price of polystyrene is and then to find out what the price of monomer is in your country, delivered to your plant. If a differential of 7 cents to 10 cents a lb. does not exist, it would be unwise to enter into a consideration of a polymerization plant.

If the volume that you believe you could capture of the polystyrene market in your particular country is at least 10 million pounds, I then believe you might want to consider the installation of a Process C, where you might grow with the business, however it would be difficult to establish a market and to keep it and grow, just having one type of material. Scheduling would be important for different grades. For crystal and impact two towers would be best, one for different grades of each type. In a big multi unit of Process C the best efficiencies would be a unit for each grade of crystal and impact you would make. However, in an imaginative run suspension process, as many as six or seven types could be run on a two kettle system with the required auxiliary equipment. In every polymerization operation, some contamination occurs. This should be kept to a minimum. However, a utility grade in your line allows you to work off any off grade or mistakes and increases efficiency. Providing the economic considerations and the outlet of polystyrene are still attractive and you would like to make a decision, it is a privilege to present to you, two packaged proposals that have been prepared, which when erected can run and produce materials of every type that were mentioned above. An estimated cost of the erection of these units in your country is concluded in the final slides. Figures

In reference to know how and royalty payment, Process C is 2% on sales for 10 years with an initial $20,000.00 payment applied to royalty for each process line. The suspension know how for crystal and for impact polystyrene on a forty million pound plant would be on the order of $50,000.00 for crystal and about $80,000.00 for impact polystyrene. A royalty arrangement on suspension would be $5,000.00 down per kettle installed, plus 0.1 cent lb. on crystal and 0.15 cent lb. on impact per year for five years. These figures do not include the erecting or the operation of the plant, but in both instances include start up help.

In conclusion, I would like to state that I have received a great deal of help in preparing this paper especially from Sam Leonard and Hector Lazzarot of the Polymer Corporation in reference to Process C and from the Pfaudler Corporation especially Mr. Culotta and Mr. Pike. However, I would like to say that the interpretation, presentation and the selection of material were my own with the editorial help* of the people mentioned above.

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*) Your attention is called to numerous patent disclosures such as the use of tertiary butyl catechol, certain catalysts etc. and these should also be considered.

FIGURE I

STYRENE HISTORICAL HIGHLIGHTS

Year	Who	What	References
B.C.	Unknown	Storax Gum	
1831	Boastre	Isolation Styrene Monomer	J. Pharm. Chim. 17 338
1839	E. Simon	Polymerization to "Styroloxide"	Annalen Vol. 31 265-277
1837-44	D'Arcet; Mulder Gerhardt; Glenard Boudault	Hot Tube Polymerizations	Various
1845	Hoffman and Blyth	Sealed Glass Tubes	Annalen <u>53</u> 314
1900	Kronstein	Closed Vessel	Ger. Patent 17,378
1911	Matthews	Thermal and Catalytic Poly for Comm. Products	Brit. Pat. 16,277
1914	Stobbe; Posnjak	Viscosity Measurements	Ber. 47 2703
1922	Moureau, Defraisse	Inhibitors	Com. Rend <u>174</u> 259
1911-1930	Ostromislensky*	Mechanism	J. Russ. Phy. Chem. Soc. Vol. 44 204
1925	Naugatuck	Commercial Prod. Monomer	
1940	I. G. Farben Ind.	" " " 600 tons month"	Ger. Plastics Practices DeBell
1930-40	Staudinger	Chain Reaction Mechanism	
1937	Dow	U.S. Polystyrene Styron	Dow Publication
1938	War Production Board	Styrene Monomer for Synthetic Rubber	Gov. Publ. U.S.A.

*U.S. Pat. 1,541,175-6; 1,613,673; 1,683,401-2,3,4,5

FIGURE II
USA

POLYSTYRENE PRODUCTION HIGHLIGHTS

			Lb./Yr.
1938	Monsanto, Dow Union Carbide	Crystal	200,000
1946	Crystal and Blend Impact		50,000,000
1961	Various types and makers	Crystal, graft Impact blends ABS	1,000,000,000
1966	" " "		2,000,000,000
1969	ABS-Impact-Crystal		3,000,000,000

PROPERTIES VS MOLECULAR WEIGHTS

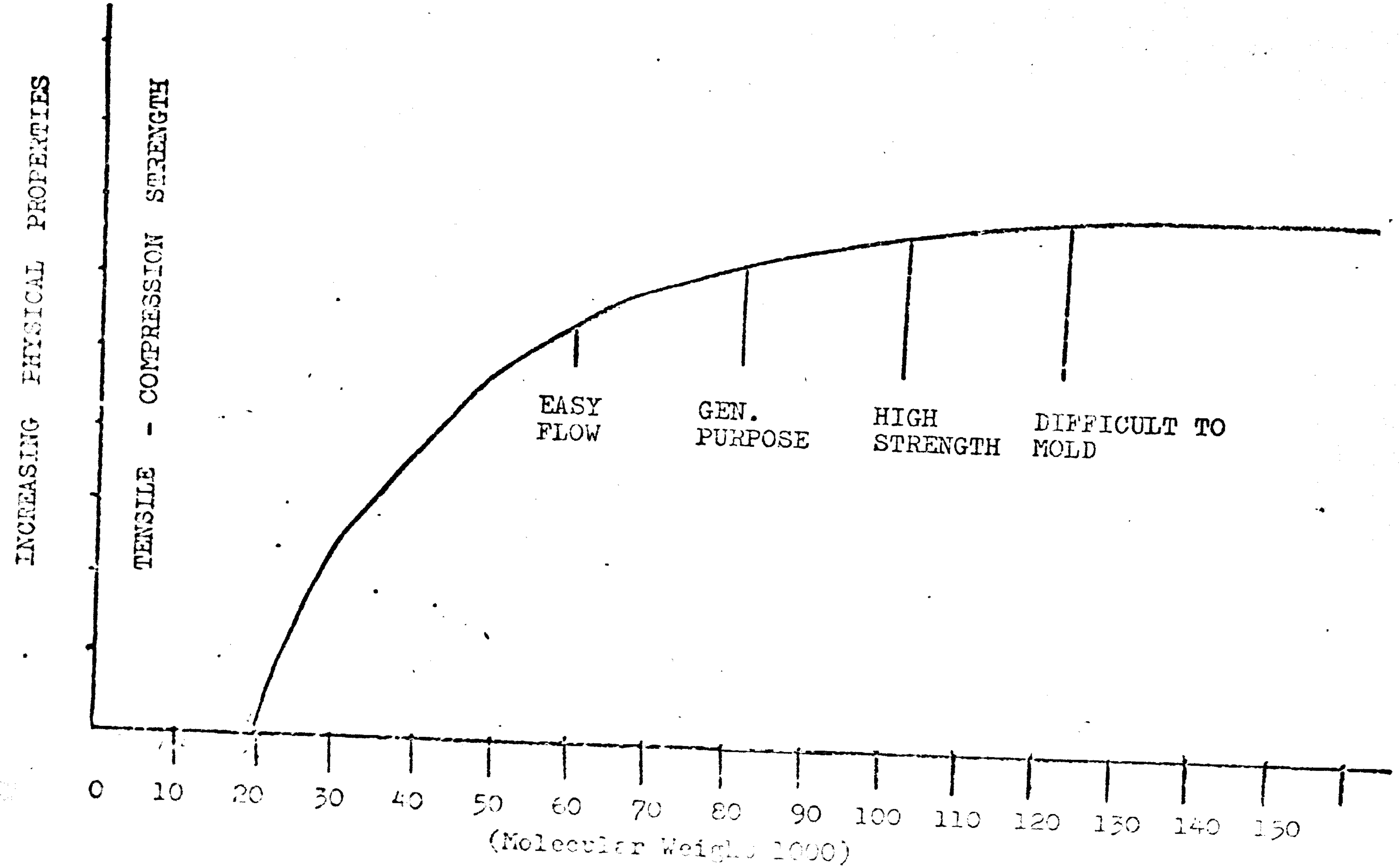
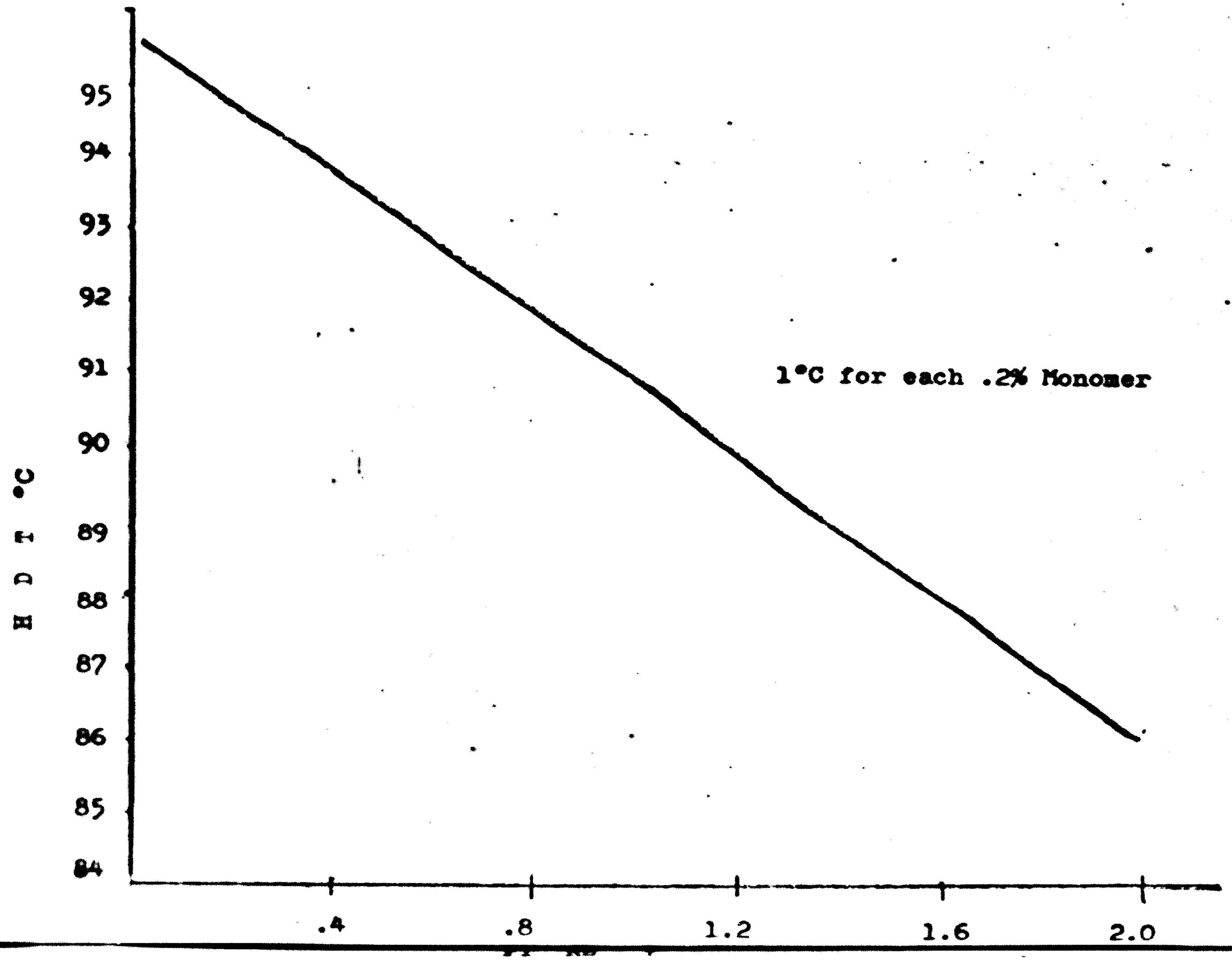
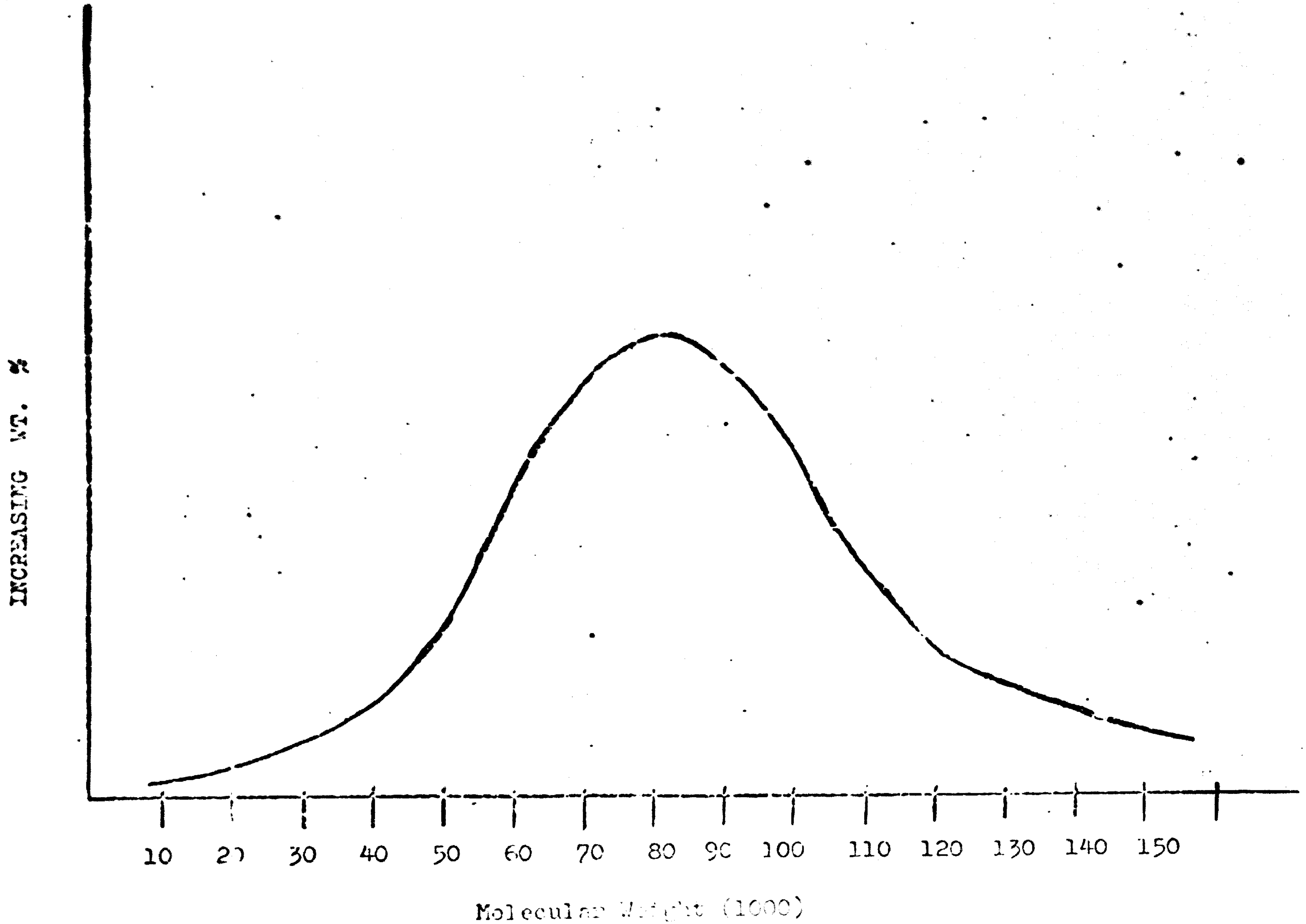


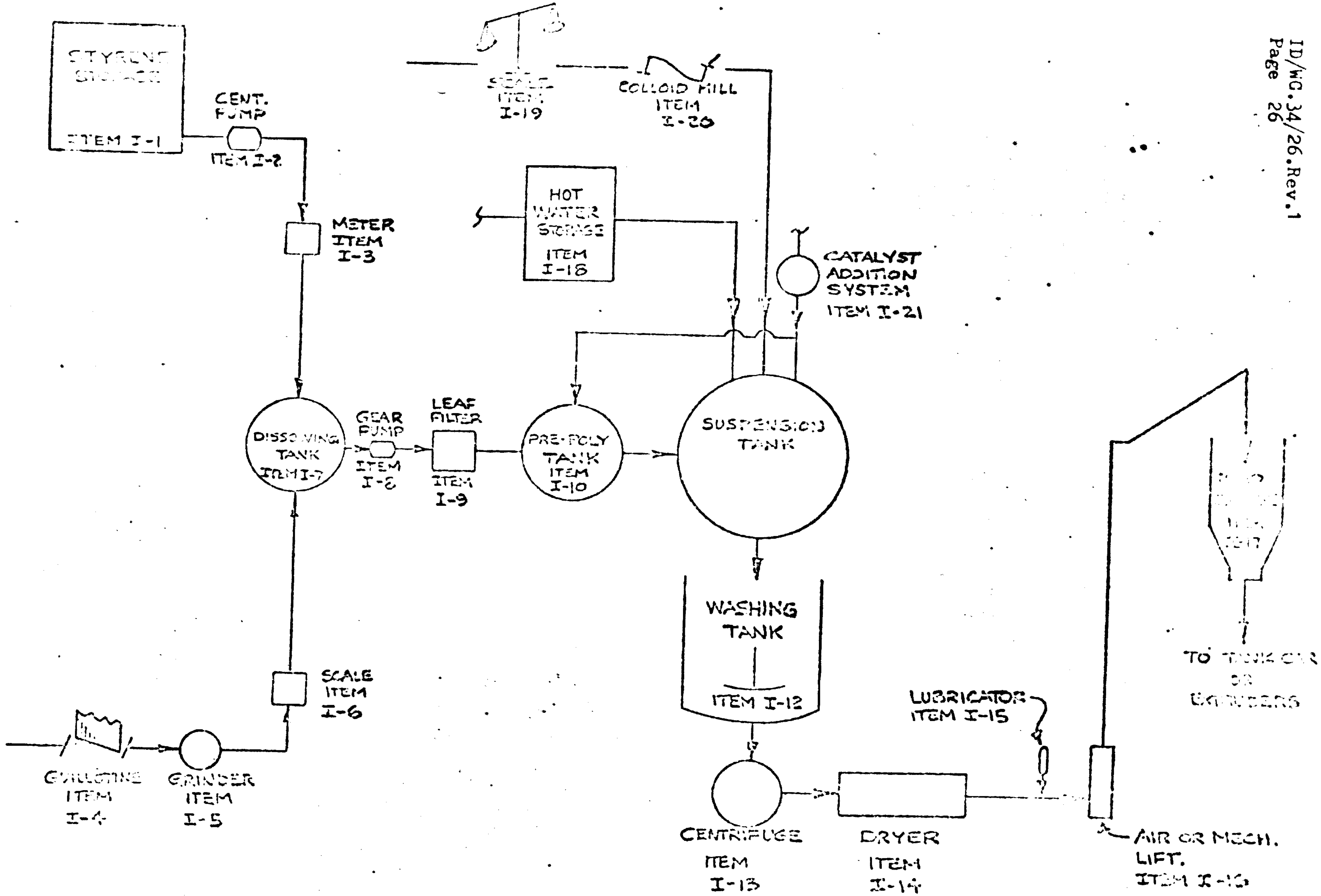
FIGURE IV

HEAT DISTORTION TEMP. VS. % MONOMER

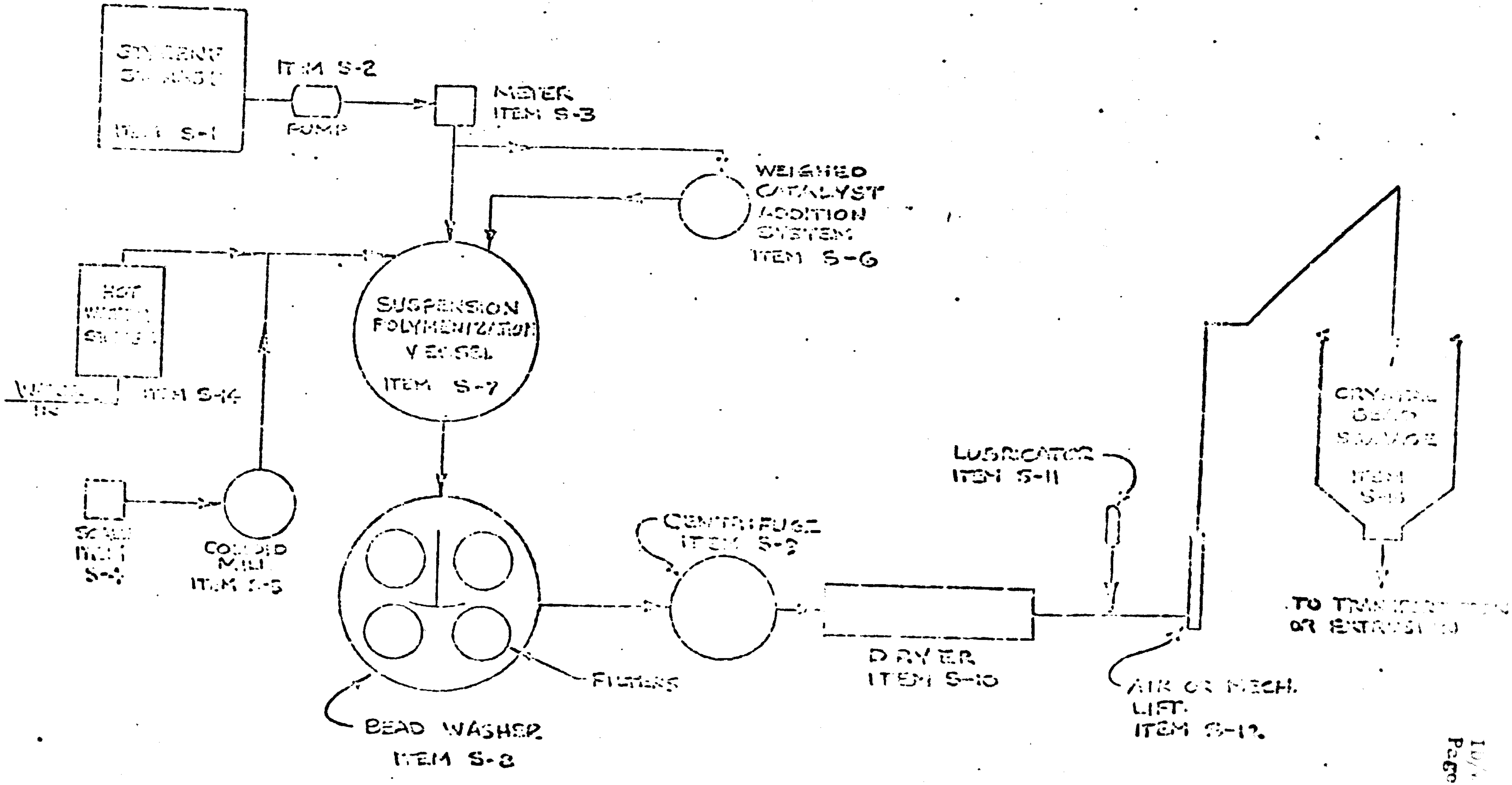


MOLECULAR WEIGHT DISTRIBUTIONS

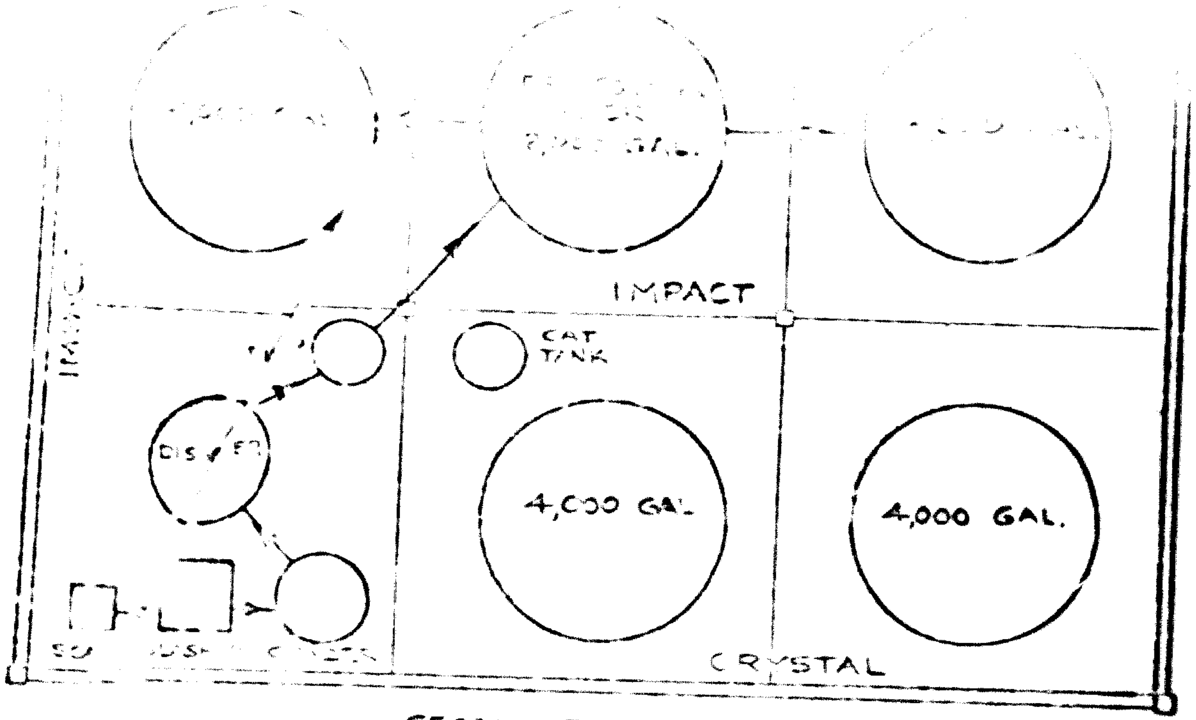




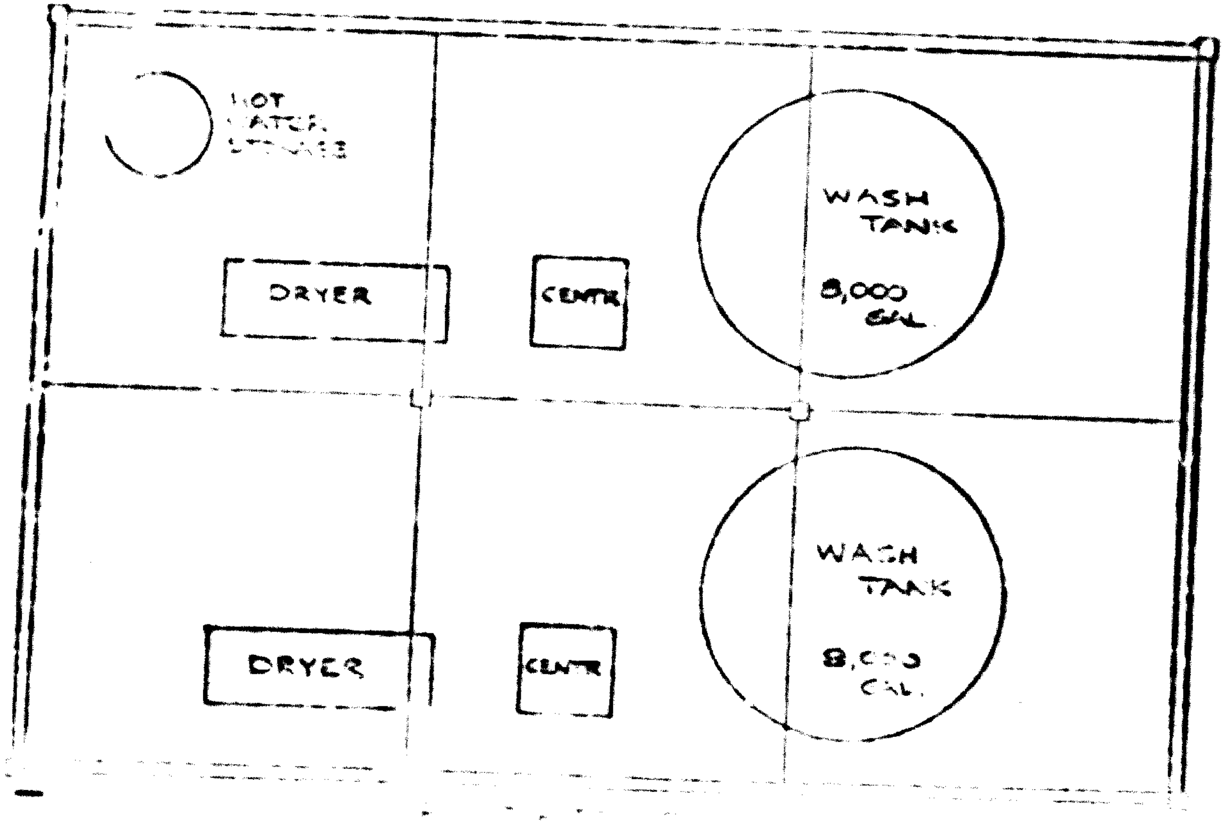
IMPACT SUSPENSION FLOW DIAGRAM



CRYSTAL SUPENSION FLOW DIAGRAM



SECOND FLOOR PLAN



[illegible]

4,000 GAL. [illegible] - [illegible]
* HEIGHT : [illegible]'-11½"
WIDTH : [illegible]' APPROX.
STIRRER HEIGHT : 13'
WEIGHT-TOTAL : 6[illegible],000 [illegible]

BASIC BUILDING - 32' x 48'

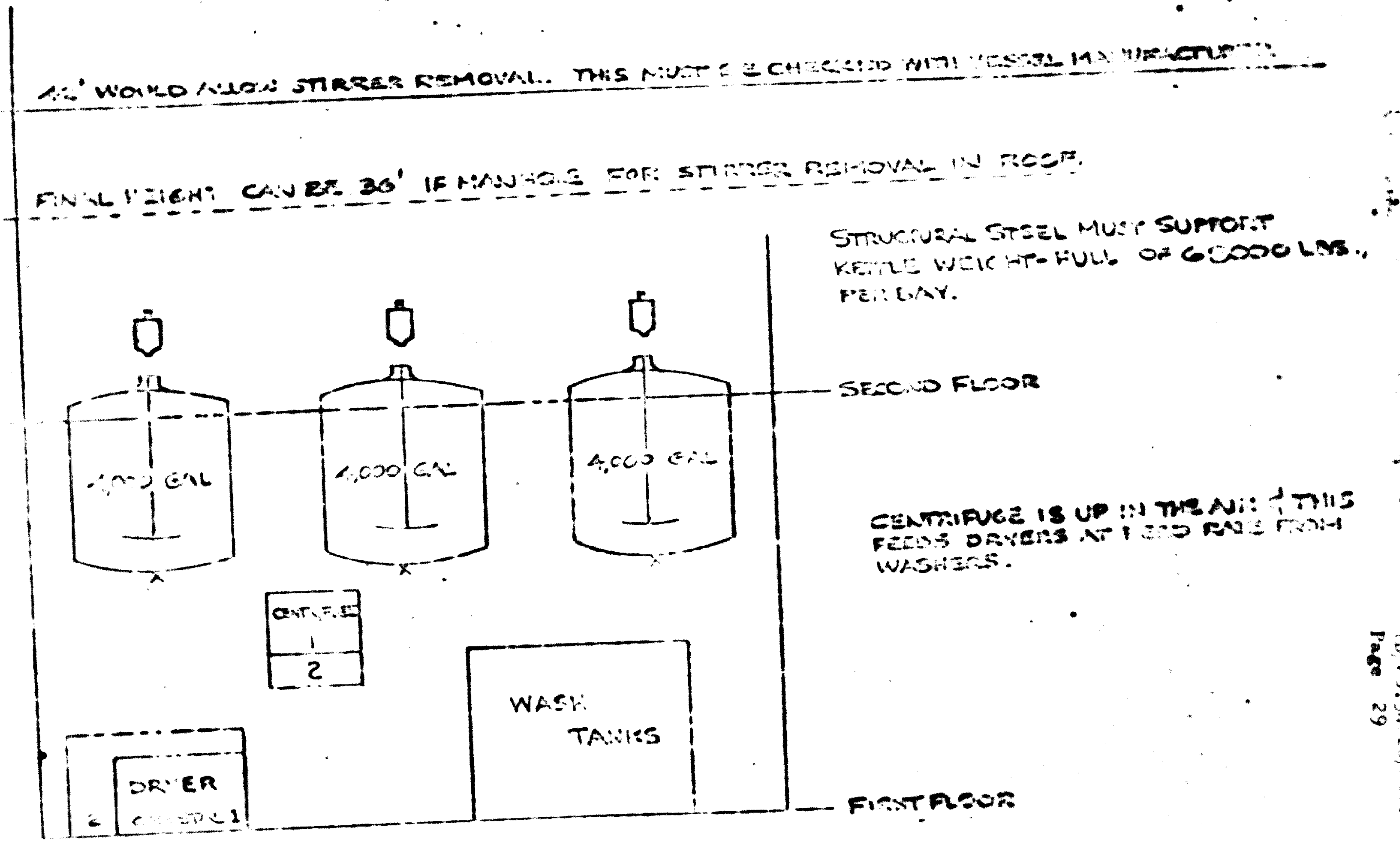
STORAGE - [illegible]LY LOCATED
OUTSIDE OF BUILDING

* WITH BOTTOM VALVE

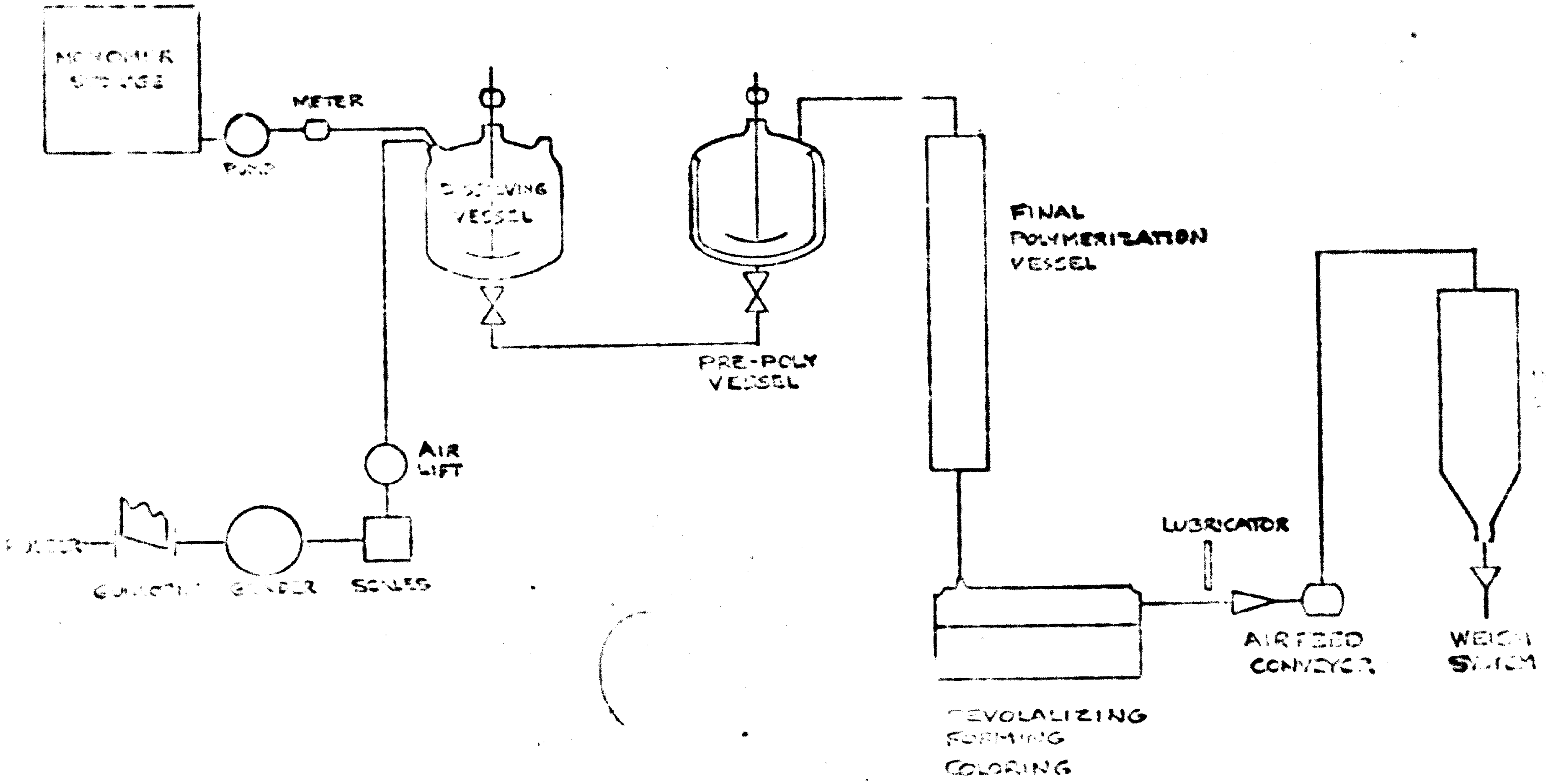
FLOOR AREAS

IMPACT & CRYSTAL BUILDINGS

FIGURE IX



ELEVATION PLAN.
IMPACT & CRYSTAL BUILDING



CONTINUOUS POLYMERIZATION PROCESS C

FIGURE XI
CRYSTAL POLYSTYRENE COMPARISON COSTS
Cent/lb.

	SUSPENSION	PROCESS C	DIFFERENCE	REMARKS
	Crystal	Crystal	Crystal	
r (1) Susp. 99% yield Proc. C 98%	8.33	8.42	+ 09	Lower Yield Proc. C
ls (2) Not in Product	.17 - .38	nil	-.17 to -.38	Suspension cost are in Catalyst Suspending Agents and [illegible] H_2O
ls in Product	.01 - .15	.02 - .14	nil	
Elec. 1.50cent KWH Steam 1.00/1000 lb. ling H_2O 22cent 00 gal.	.323 - 343	.19 .035 .09 .3	-.025 - .033	In suspension H_2O goes along for ride
r $6,000/yr.	.48	.33	-.15	devolatilized from reactor and reduces manpower
and Maintenance	.12	.12	nil	
l Laboratory	.20	.06 - .1	-.1 to -.14	Quality Control cost depends on effort
tion 7 yr. st line	.45	.57	+.12	Proc. C not opt.
Costs 2 to 8	1.75 - 2.12	1.41 - 1.57	-.235 to - 493	

[illegible] U.S.P. [illegible] cent lb.
[illegible] cent lb.
[illegible]

Proc. C has not been optimized and
production per unit [illegible]

FIGURE XII

IMPACT POLYSTYRENE COMPARISON COSTS

CENT/LB.

	SUSPENSION	PROCESS C	DIFFERENCE	REMARKS
	Impact	Impact	Impact	
Monomer (1) Susp. yield 99% Proc. C yield 98%	8.33	8.42	+.09	Lower yield Proc C
Chemicals (2) Not in Product	.58 - .67	nil	-.58 to -.67	Suspension cost are in catalyst suspending agent and Demin water
Chemicals in Product	.81 - 1.68	1.0 - 1.7	nil	
Utilities Elec. 1.50 cent KWH Steam $1.00/1000 lbs. Cooling Water 22 cent 1000 gal.	.415 - .45	.225 .025 .09 .34	-.075 to -.11	In suspension H_2O goes along for the ride
Labor $6,000. yr.	.52	.33	-.21	Does [illegible] from reactor and reduces manpower.
Repairs and Maintenance	.14	.14	nil	Quality control depends on effort
Control Laboratory	.20	.06 - .12	-.08 to .14	
Depreciation 7 yr. st line	.50	.67	+.17	Proc. C not opt. yet
Production Costs 2 to 8	3.165 - 4.16	2.54 to 3.30	-.625 to .87	

Styrene Monomer U.S.A. 8.25 cent/lb.
Chemicals Cost Bz_2O_2 92 cent/lb.
di Bu_2O_2 $3.00 lb.
TCP 9 cent lb.
Demin. H_2O
[illegible] lb.
[illegible]

25. I. 72