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D04558



United Nations Industrial Development Organization

Distr.  
LIMITED

ID/WG.137/65  
25 January 1973

ORIGINAL: ENGLISH

Symposium on the Development of the Plastics  
Fabrication Industry in Latin America

Bogotá, Colombia, 20 November - 1 December 1972

PLASTICS TOMORROW - MATERIALS AND TECHNOLOGY

"Plastics Preview for the 1970's"

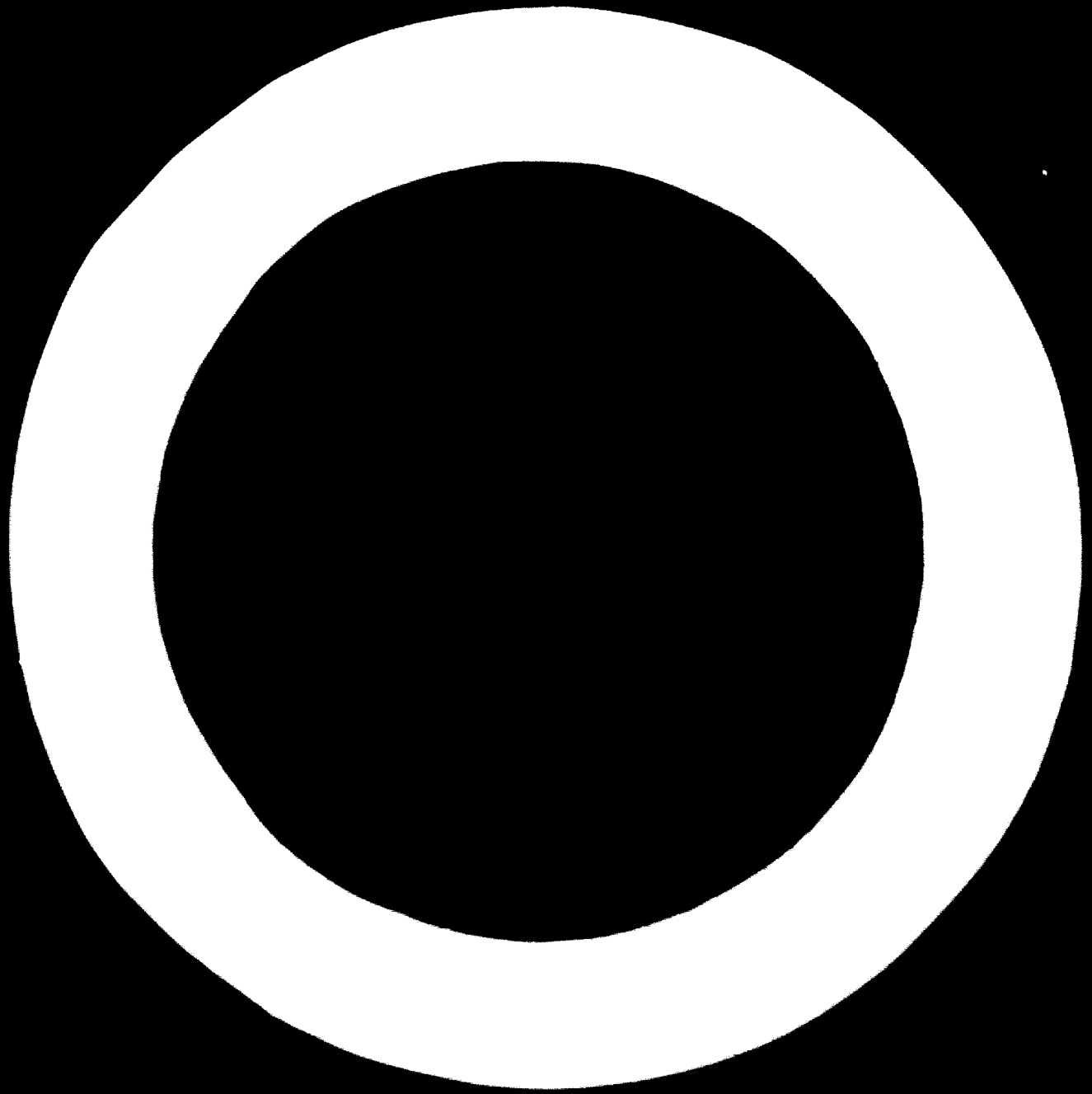
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id.73-503

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## INTRODUCTORY LECTURE

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### "PLASTICS PREVIEW FOR THE 1970'S"

#### 1. Introduction

Progress in any industry and specifically in the chemical industry is governed by two factors: new materials and new techniques.

One purpose of this UNIDO symposium is to unfold to potential investors a picture of the present state of the plastics industry in the Latin American nations and of its capacity to establish attractive and profitable business. The program lists for this purpose first about 20 reports of the individual countries in the Latin American World to describe their operations, planning and problems. Then, an equal number of distinguished visitors from highly industrialized nations are going to present their approaches and their points of view to the same problems.

Investors, however, are not satisfied with a short range forecast for their installments--they want to be safely informed on the probable course of events over a longer period--say 5 to 10 years. Dr. H. May of UNIDO, who is the Director of this Symposium, has, therefore, asked me to discuss with you those new materials and novel techniques which are going to cooperate with the existing ones to pilot our industry during this decade.

All of them--materials and techniques--are still in a pioneering state and the new products emerging from them are not yet available on a large commercial scale but rather in experimental quantities only; these are now used to explore future markets and to establish preferred specifications.

## 2. New Materials

Table 1 shows a few new materials--i.e. new chemical compositions-- which are now subject of intense R and D efforts in Government Laboratories, University Institutes and, most of all, Industrial Organizations. Let us, briefly, discuss each of them and indicate its probable impact on the plastics industry.

Normal polymerization reactions, as they are presently used, f.i. for the production of PVC in emulsion, PP in suspension or PSty in bulk require several hours to reach a conversion which permits economic production of the goods. Recently a system was developed which completes polymerization (to more than 99%) in a few hundreds of a second. It consists of an acrylic composition which contains a thickener and a sensitizer (optionally also fillers, pigments, flame proofing and antistatic agents) and a commercial UV lamp which permits irradiation of the mixture in the form of a fiber or film at short range (1 - 3" with about 100 watt). The viscous mass hardens within fractions of a second--nothing is added, nothing comes off; it is the direct, rapid, solventless conversion of monomeric units into a polymer in its final commercial shape--fiber, film, laminate, adhesive etc.

Any standard solution spinning needs removal of substantial quantities of the solvent and sometimes also of the spinning bath and is always prone to come in conflict with environmental protection. Melt spinning is only possible for fusible polymers and, in most cases, requires the separate preparation of the thermoplastic polymer, its subsequent melting and spinning. The new method can be carried out with thermoplastic and thermosetting compositions, involves only one continuous operation and is free of any pollution hazards. There exist already several embodiments of this system

approach in an advanced pioneering stage, such as the rapidly setting paints of DuPont and PPG, the solventless primerization of automobile parts by Ford and GM, the varnishing of plywood by Boise Cascade and Champion International and, more advanced, the Visa process of Deering Milliken and the Suncure system of Sun Chemical<sup>(1)</sup>.

Up to the late 1940's the highest melting or softening points of thermoplastics were around 300°C; Teflon, the epitheton of stability at high temperatures melts at 328°C. In long range exposure all known plastics would deteriorate thermally or chemically already between 150 and 170°C. At that time Professor C. S. Marvel, then at the University of Illinois, advanced the idea that the systematic incorporation of aromatic units in a linear macromolecule would increase its stability at high temperatures, raise its modulus of rigidity and still maintain a high level of toughness. In fact, the first representatives of these polyaromatic systems which were prepared in his laboratory proved the point to such an extent that an important new branch of polymer science and technology developed from his concept.

Today, several thousand individual compounds of this type have been synthesized by a small army of polymer chemists in all industrialized countries. Initially they were delicate to make and difficult to handle. Consequently they represented expensive laboratory curiosities which could only be applied in small quantities at strategic positions in rocket engines, space vehicles, supersonic aircraft and micronized electronic equipment. But the skill and perseverance of the chemists, physicists and engineers, who continued to work along these lines, gradually rendered them more accessible and more tractable. As a result, many representatives of this new class of organic polymers are now becoming available in the form of fibers, films, coatings, adhesives,

winding dopes and heat settable molding powders.

Examples for fibers are Fiber B and PRD-49-Type 3 of DuPont which render excellent services as cords for radial tires and as yarns or fabrics for the reinforcement of plastics. They are highly oriented para-aromatic polyamides with a specific gravity of  $1.3 \text{ g/cm}^3$  and a softening range above  $550^\circ\text{C}$ ; Fiber B has a modulus of about 450 g/den (9 million psi) a tensile strength of 12 g/den (450000 psi) and an elongation to break of 7 - 8%. PRD-49, which is more highly oriented has a modulus of rigidity above 1000 g/den which corresponds to 20 million psi and is superior to the modulus of E-glass and S-glass filaments. The strength of PRD-49 ranges up to 25 g/den, its elongation to break is still about 2%. Since it is of organic chemical character it binds very well with a thermosetting resinous matrix and is remarkably stable to corrosion. It appears that, on account of all its properties PRD-49 will emerge as the best presently available filamentous material for the reinforcement of thermoplastic and thermosetting resins and even for the stiffening of certain metals. Fibers of similar character are also pioneered by other companies in the industrialized nations such as Monsanto, Carbide and Carbon, Akzo, Bayer, ICI and Mitsubishi; some of them are even more highly condensed aromatic systems such as polyimides, polybenzimidazoles, polyoxadiazoles, polysulfodiazoles and polyquinoxalines. Most of these materials are now pioneered in the form of fibers or films (Kapton of DuPont) and softening ranges as high as  $700^\circ\text{C}$ . In fact, upon heating they do not really melt but carbonize and, at still higher temperatures, graphitize. In this way they form the transition to the infusible and insoluble graphite fibers--Thornel of Carbide and Carbon Company and Modmor of Morgan Crucible Ltd.--which have moduli above 100 million psi (higher than steel), tensile



strengths above 500000 psi and still a specific gravity as low as 1.4 and a complete resistance against corrosion. At present, they are high priced specialties but their precursors are inexpensive and improvements of their preparation are in sight and some producers are looking forward to selling prices of \$4.00 to \$5.00 per lb. (2)

Another area in which organic polymers start to approach the performance of inorganic systems--in this case the packaging services normally rendered by glass--is the successful pioneering of thermoplastics, which are hard (modulus of rigidity above 400000 psi), tough (impact strength above 3 or 4 ft.bl./inch), colorless, completely transparent, impermeable to gases and acceptable to the Food and Drug Administration for the packaging of all kind of beverages from whiskey and gin to coca cola and all carbonated soft drinks. Over glass they have the advantage of light weight (specific gravity around 1.2 against 2.5), unbreakability and removability by combustion.

The leading compositions in this field are acrylic - vinyl copolymers or terpolymers with acrylonitrile, metacrylonitrile, styrene and acrylicesters as principle components. Barex of Sohio, Lopac of Monsanto and SM-resin of DuPont are blown into specially designed bottles by major packaging firms such as Continental Can Company and are presently undergoing large scale field testing in the USA. The compositions do not contain chlorine and only minor percentages of nitrogen. As a result they can be used as disposable, one way bottles because, after collection, they can be destroyed by combustion in standard incinerators together with other refuse such as paper, cardboards, wood, textiles and with all organic waste from food such as bones, vegetables fruit, fat and proteins. (3)

These plastic bottles and many other disposable items such as cups, plates, dishes and bags pose another important problem to the protection and cleanliness of our environment. Sure, if these objects are properly collected and adequately processed by incineration, they can be handled like any other city refuse; they even burn much more readily than moist paper, wood or food waste. But, the trouble is that they are not always collected but negligently thrown away on roads, in picnic areas and at camping places. The efforts to combat this inconvenience started by dividing plastics into two categories: those which should last as long as possible and those which should be readily degradable.

To the first class belong all plastics which are used in the building and servicing of airplanes, cars, buses and homes. Examples are the polyolefins, vinyls, acrylics, polyesters and polyurethanes which are used in paints, dash boards, door handles, water pipes, floor covers, ventilation ducts, roofing and siding of houses. They should perform their services as long as possible with no loss in properties. On top of the natural stability of many plastics--polyethylene, polyacrylics, etc.--one adds small quantities (usually about one percent) of stabilizers which can either be only physically admixed or chemically bonded to the polymer. This principle of stabilization is known since long and there exist for each plastic system a reasonable selection of stabilizers which may not be completely satisfactory in all cases but, in any event, represent a step in the right direction.

The second class of plastics are supposed to serve only a short time--months or even only weeks--they are the disposable type as originally existing as paper or cardboard and now being represented by bags, wrappings, cups, lids and many other objects made essentially of polyolefins and vinyls.

They should not last but disappear as soon as they have served their short range purpose. This problem is important for environmental cleanliness and has, therefore, been recently attacked in a systematic manner by the search for additives which would make these plastics selfdegradable and biodegradable under ambient conditions of sunshine, rain and the presence of microorganisms. In principle, there exist degradizer for plastics just as stabilizer and the ultimate selection of a sufficiently active system of them is only a matter of adequate and patient research. Efforts in this direction have been started by several organizations in the industrialized countries, particularly the USA, Germany and Japan. As a result, there exist now certain degradable species of polyolefins, polystyrene and PVC which disintegrate into a powderous mass under the influence of ambient weather conditions within several weeks and, eventually, are taken care of by microbes so that virtually nothing is left after several months. Whether this degree of degradability is sufficient for practical purposes remains to be seen; the present field tests will establish the degree of success and may well necessitate additional efforts in this direction. (4)

There are other areas of R and D where new chemical compositions have been introduced and where now improvements and refinements are looked for.

One is the use of organic polymers for medical applications in the form of hard implants to replace bones and to heal injuries in a new and efficient way. Even more important are soft implants such as membranes, capillaries, tendons and plastic lenses. There exist also many interesting applications of soluble polymers in the form of blood plasma extenders or substitutes and as insolubilized or otherwise manipulated enzymes, antibiotics

and prostaglandins. It would surpass the limits of this report to describe in detail present activities in this area and it may suffice to add here a few literature references. (5)

The same is true for recent attempts to use organic plastics not as insulators--as usual--but as conductors and semiconductors, where they excel by their light weight, their resistance against corrosion and the wide variety of properties which can be imparted to them by relatively simple treatments. (6)

### 3. New Techniques

As long as synthetic fibers were mainly made for the use in textile industry the modern, sophisticated looms and knitting machines placed stringent demands on all properties of the yarns, particularly on uniformity in mechanical and tinctorial respect. These demands in turn require very carefully controlled filtration and impose on the operation limited spinning and drawing speeds. This affects unfavorably the productivity of a given spinning unit.

As a result of this situation it appeared worthwhile to explore what kind of fibers one could make and what efficiency one would get, if one would not want the material for classical textile uses but, f.i., only for the purpose of making a felt or a non woven web, where uniformity would play only a very minor role. This led, some 20 years ago, in the DuPont Pioneering Research Division to the study of flash spinning where polymer solutions or melts are extruded at very high speed (up to 4000 m per minute from a large number of holes--500 - 2000) and not collected on a spool or a reel but, instead deposited as a loose, fluffy layer on a moving belt. The emerging filaments are immediately exposed to the shearing effect of even more rapidly moving air which causes an exceptionally high degree of orientation and, if the material is crystallizable, a correspondingly high degree of crystallinity. Hence,

the fibrous fluff on the transport belt--the so-called fibrids--are extremely fine and possess exceptionally high rigidity and strength; they may consist of one single material such as polyethylene, polypropylene, polyamide, polyester, etc. or they may be a blend of two or more individual materials. The fluff on the belt is first compressed between rolls to a higher density and finally bonded together by heat sealing of the individual endless filaments between heated rolls. Low melting plastics like polyethylene or polypropylene may be heat sealed directly; higher melting species require the addition of a small amount (5 - 10%) of a heat sealable component.

The final spunbonded sheets may be very loose--like a lace with 10 g/sq.m or very heavy, like a felt with 300 g/sq.m or anything in between. Several companies are pioneering this field: DuPont with polyethylene (Tyvek), polypropylene (Typar) and polyester (Rieman); Monsanto with polyamide (Cerex), The Oe SW in Austria with polypropylene and several companies in Japan and Europe with various polymers.

The resulting sheets are extremely strong, tough, dimensionally stable and maintain their properties even in the soaking wet state. Applications range from wall paper over outdoor signs and posters to maps, envelopes, table cloths, carpet, curtain and fabric backings. These plastic webs are not only used alone but can also be placed as a very thin lace between two cellulosic tissues with the aid of a standard paper machine to produce a triple layer sandwich, where the outer layers are soft, moisture absorbing cellulosic tissues whereas the center is a polyethylene web which gives the composite system a remarkable strength and dimensional stability even in the soaking wet state. The Crown Zellerbach Company is pioneering products of this type under the name of Crowntex. Tough, rigid and opaque

sheets of paper-like character can also be made by the extrusion or blow molding of polyblends f.i. of a mixture of 60% high density polyethylene and 40% impact polystyrene; they do not have quite the strength and toughness of the spunbonded webs but are opaque, printable, pliable, moisture insensitive and are now studied, particularly in Japan to use them for telephone books, catalogs, railroad and airplane timetables and similar applications. Altogether these new techniques are promising to find new, large scale commercial outlets for polyethylene, polypropylene and polystyrene.

Fiber spinning traditionally is carried out by the extrusion of a polymer solution or a polymer melt through fine capillaries with subsequent drawing and twisting of the resulting threads. Certain plastics, however, have such high melt viscosities that they cannot be moved through narrow paths without danger of obstruction or melt breaks. However, these melts may be readily extruded through a slit or hopper which offers much less resistance than a fine cylindrical tube. In other words: one can often make a film even if one cannot make a fiber. But a film is as good as a fiber because a process has been worked out to slice the film into narrow (2-4 mm) ribbons, stretch these ribbons over a blade to a draw ratio of 7 or 8 to one and twist the resulting highly oriented thin and narrow band until it breaks up into a fibrillated structure which has high rigidity, high strength and a remarkable crimp.

This film to fiber conversion can also be used for a laminated film which consists of two layers e.g. half of polypropylene and half of 6-nylon. The fibers made from such a film are "side by side composites" which combine the structural and chemical properties of its two constituents and have, above all, a crimp of truly permanent resilience.

Again, this new technique uses old and well known polymers but, by its special way of compounding, opens new channels for the use of already existing materials. Film to fiber conversion is of special importance for polymers which cannot be dissolved and not be conveniently fused. In the case of Teflon f.i. Dr. H. Kraessig prepared blocks of this material by sintering a fine powder at elevated temperatures under pressure, shaved off thin (about 5 mils) sheets and submitted them to the film to fiber conversion process. He obtained, at the end, fine and uniform Teflon filaments which had considerable strength and toughness. Another technique which deserves interest and is making significant progress is the dry powder coating method. Traditionally coatings for protective and decorative purposes are deposited either from the solution of a polymeric system in an organic solvent or from a suspension or emulsion of such a system in water. In both instances a relatively large amount of waste byproduct is formed; in the first case one has to take care of a more or less volatile and flammable material which must be recovered wither for economic reasons or, in any event, in order to minimize air pollution. In the second case - electrodeposition from aqueous baths - large quantities of waste water result which pose a difficult problem of recovery and/or purification. Dry powder coating eliminates all these difficulties and is, therefore, a technique on which considerable efforts are now being concentrated. An important requirement is the availability of fine, uniform powders of those polymeric compositions, which are going to be used to produce the film, which must be hole-free, of uniform thickness and flawless appearance. Even though these compositions, as such, are not new - polyolefins, vinyls and acrylics - they ought to have certain special characteristics, such as narrow molecular weight distribution, ready flowability and good

adhesion to the substrate. As an example of a specially designed material for the dry powder coating technique a polypropylene of Hercules Chemical Company should be mentioned which successfully combines the essential qualities which are necessary for this novel method.

Much interest is presently devoted to the use of polymers in biochemistry biology and medicine and new materials as well as new techniques are being developed in order to put synthetics to work in these important and progressive fields. A specific technique which has already rendered interesting results and, apparently, holds considerable promise for the future is the manipulation of enzymes and antibiotics. It has been found several years ago that certain reactive groups of proteinic substances, particularly the amino- and carboxyl groups can be used to graft synthetic polymers - vinyls, acrylics, polyesters, polyamides, etc.- onto the protein and embed it into a matrix of synthetic material. The proportion of the original protein and the added synthetic may be varied over a wide range and includes compositions which are "half" natural and half synthetic. A new and, apparently, very attractive fiber - Chinon of the Toyobo Company in Osaka - represents an embodiment of this idea. It consists of a graft of about 50 parts of acrylonitril on 50 parts of a fiber spun from regenerated soyabean protein and combines the strength and toughness of acrylic fibers with the moisture metabolism and tinctorial properties of silk.

If the proteinic substance is an enzyme or antibiotic its specific activity is not seriously affected by the chemical combination with the synthetic matrix but its physical properties such as solubility and state of aggregation are completely changed. If one, for instance, grafts 50 parts



of polystyrene on 50 parts of Chymotrypsin the enzyme becomes completely immobile in water but can be dissolved in organic solvents such as benzene or methylethyl keton and maintains a very large part of its activity in this strange and, so to speak, "unnatural" environment. In this manner, enzymatic and antibiotic activity can be transferred in surroundings where it does not occur in nature. One has also succeeded to embed enzymes and antibiotics into matrices of crosslinked synthetics, insolubilize them completely and make them permanent parts of a solid material such as a fiber, film, foam, powder or screen. In this manner the activity can be localized and fixed in a desired manner on a filter, inside of a capillary or on a surface film. The advantage of this technique is that the converted substrate is not contaminated by the remnants of the enzyme and the enzyme can be used in a continuous and reversible manner. Numerous interesting applications of this new method have been enacted and many more are still in store in the near future.

Finally, attention should be drawn to new techniques for the preparation of ultrathin membranes and hollow filaments which combine a high permeability for water with a pronounced impermeability for all kinds of solutes such as ions, inorganic molecules and organic materials of all kind. Systems of this type are of great interest for the purification of waste liquids including the reuse of industrial and urban water and for the desalination of sea water with the aid of the reverse osmosis principle. If films are employed one deposits very thin (400-2000 Å) layers of certain cellulose derivatives (acetate, propiono sulfonate) or of aromatic polyamides on a thicker (2-6 mils) porous film of a strong synthetic polymer such as a polysulfone, polyamide or polycarbonate. Compositions of this type combine a high water flux (many gallons per hr per square foot of the film) with excellent rejection of the solvent (99% and

more) and with a ratio-factory period of activity. If fibers are used one produces by solution spinning hollow filaments which consist of a very porous wall on the outer surface which there is a very thin and dense layer of the same material which is responsible for the separation. This layer is only 500-1000 A thick whereas the wall of the tubular fiber has dimensions between 1 and 2 units. A large number of those hollow filaments (up to 2 millions) is assembled in parallel configuration inside of a metal cylinder in such a manner that the impure feed flows outside of them under a pressure of several (20-50) atmospheres whereas the pure water emerges at the inside of the capillaries. Systems of this type with a capacity of several hundred thousand gallons a day are already in commercial use to desalinate brackish water and to purify aqueous industrial wastes in metal finishing and electrodeposition plants.

The straightforward desalination of sea water can be carried out by both methods but at present, costs about \$1.00 for 1000 gallons which is still about 50% above a commercial attraction price. There can be no doubt, however that additional improvements in the materials used in the design of the equipment will soon result in a way for commercial desalination of normal sea water and for the regeneration of most industrial and city wastes.

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TABLE 1

NEW MATERIALS FOR THE 1970'S

- Rapidly polymerizing (setting) compositions
- Heat resistant thermoplastic and thermosetting systems
- Rigid and tough barrier materials
- Readily degradable plastics
- Plastic system for medical uses
- Plastics as conductors and semiconductors

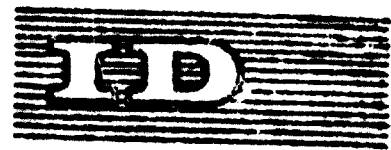
TABLE 2

NEW TECHNIQUES FOR THE 1970'S

Spunbonding and polyblending - plastic papers  
Film to fiber conversion, bicomponent fibers  
Dry powder coating  
Manipulation of enzymes and antibiotics  
Preparation of semipermeable membranes and of hollow filaments  
Preparation of springy polymers

Techniques

- 1) Spunbonding
- 2) Film to fiber
- 3) Dry powder
- 4) Enzymes
- 5) Semipermeables



Distribution  
LIMITED

ID/WG.137/65 SUMMARY  
19 November 1972

United Nations Industrial Development Organization

Original: ENGLISH

Symposium on the Development of the Plastics  
Fabrication Industry in Latin America

Bogota, Colombia, 20 November - 1 December 1972

**SUMMARY**

**PLASTICS TOMORROW - MATERIALS AND TECHNOLOGY<sup>1/</sup>**

by

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Future progress depends on the availability of new materials and on the emergence of novel techniques.

New chemical compositions which will, very probably, influence the developments of the next ten years are:

- Very rapidly setting solventless systems
- High temperature resistant thermoplastic and thermosetting compositions
- Rigid and tough barrier materials
- Weathero - and biodegradable plastics
- Polymeric conductors and semi-conductors
- Special plastics for medical uses.

Novel techniques which will permit to find new uses for existing materials include:

- Spunbonding and multiple sheet designs

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Film to fibre conversion

Manipulation of enzymes and antibiotics

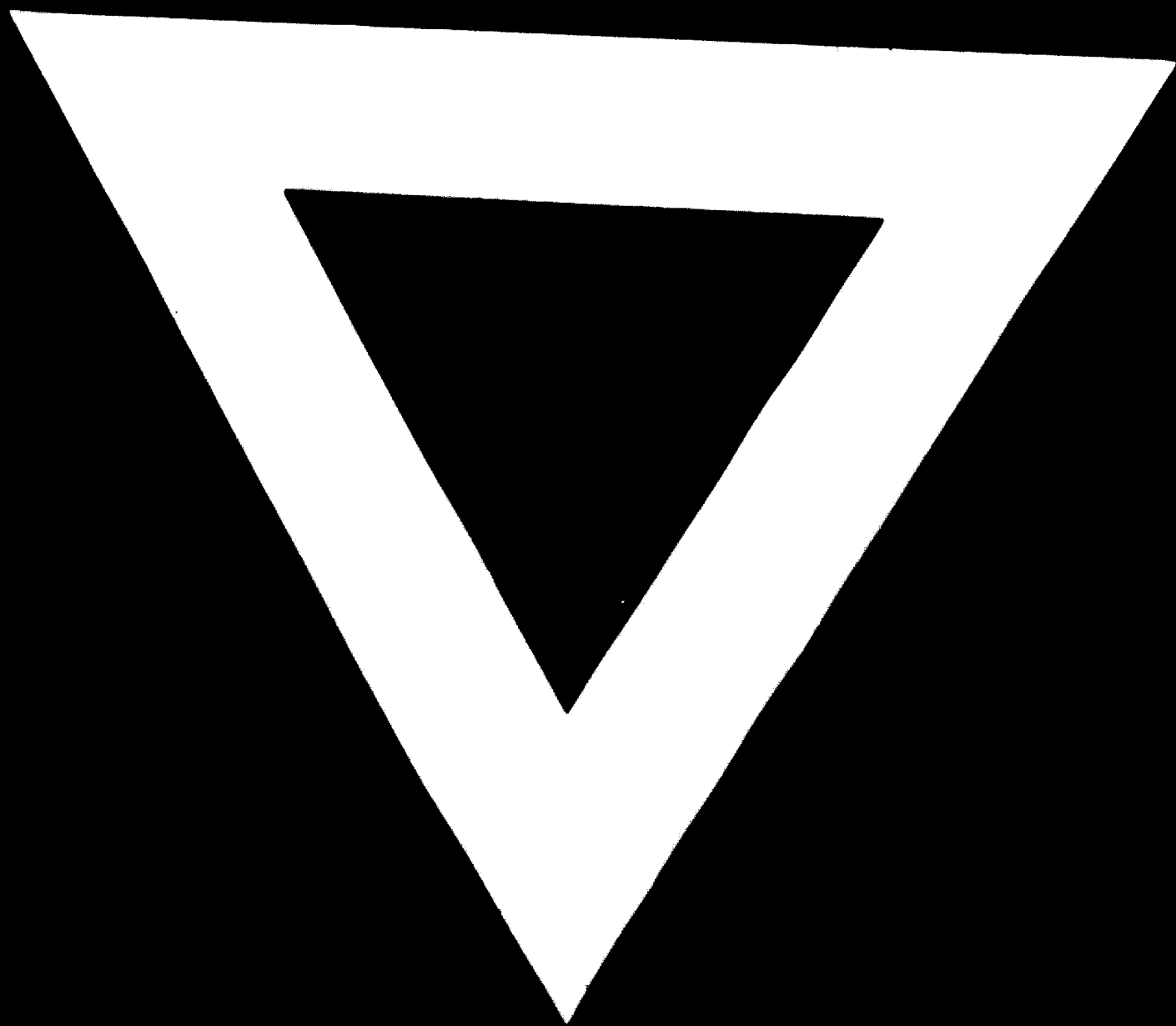
Preparation of semi-permeable membranes and hollow filaments

Preparation of springy polymers

The lecture will select a few cases and demonstrate samples which illustrate the present state and allow a forecast of probable improvements.

P. Durand	ID/WG.137/4	Nov. 21	LDPE	PE pulp
L. G. Mettes	ID/WG.137/16	Nov. 21	PRD-49	instead of glass
J. Coudenhove-Kalergi	ID/WG.137/49	Nov. 22	PRD-49	instead of glass
J. Mueller	ID/WG.137/33	Nov. 23	Sharper MW distribution and degradability	
H. Dominghaus O. Heiner Wolfgang Hofmann	ID/WG.137/12	Nov. 23	Sharper MW distribution and degradability	
K. F. Grafe	ID/WG.137/27	Nov. 23	Sharper MW distribution and degradability	
J. Zembron	ID/WG.137/36	Nov. 24	PP/PE blends	instead of PS
L. O. Philipson	ID/WG.137/10	Nov. 24	Sharper MW distribution	
D. Schleede	ID/WG.137/14	Nov. 27	Intumescent coatings	
J.M.Krause F.J.Koehler	ID/WG.137/13	Nov. 28	Sharper MW distribution and ready degradability	
L. Goiran	ID/WG.137/7	Nov. 28	Rigid and tough barrier systems	
K. Rohé	ID/WG.96/6	Nov. 28	Intumescent coatings	





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