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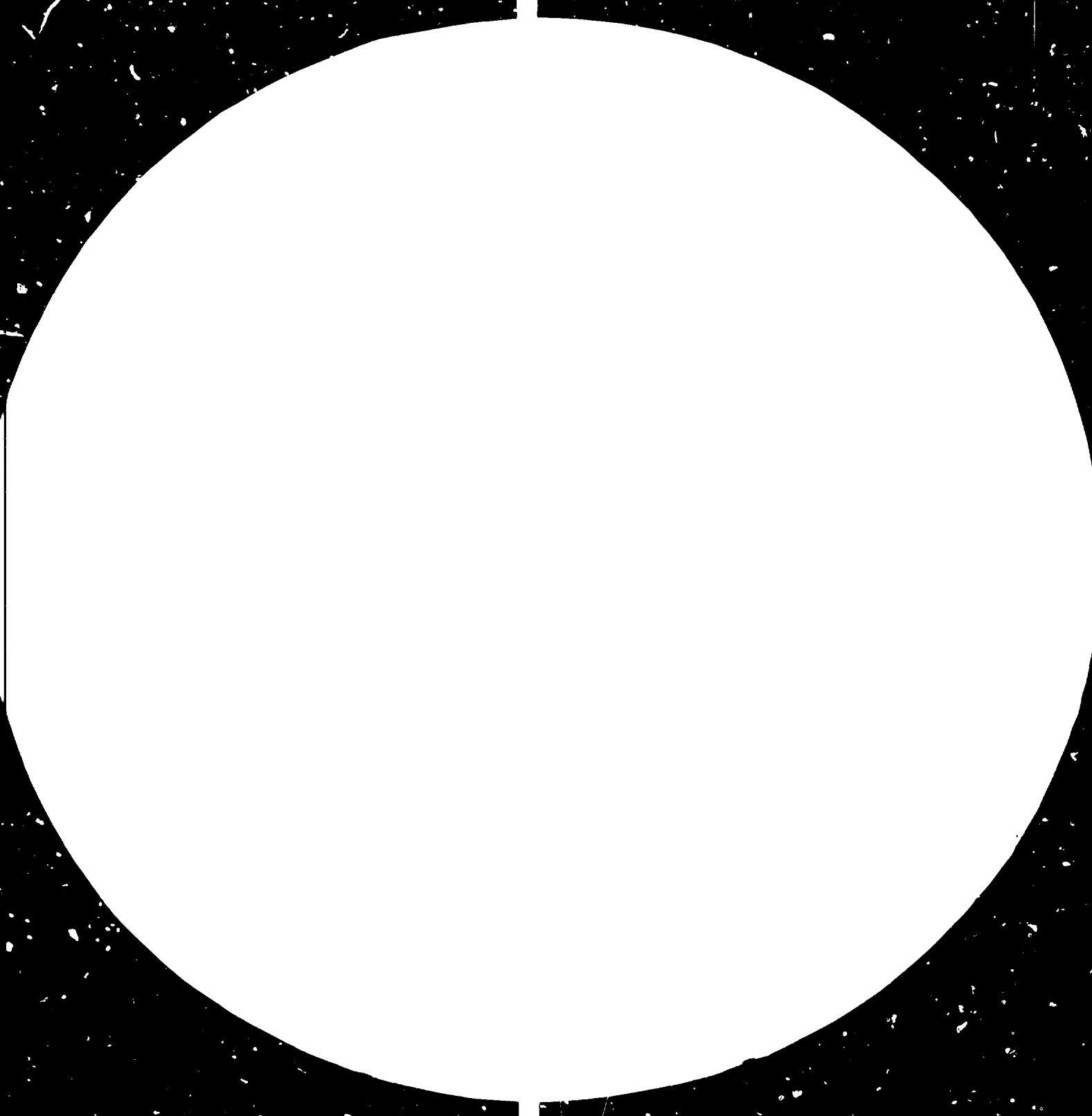
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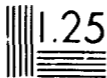
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PVC MANUFACTURE AND USES*

by

Donald H. Hunter**

00217

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** Technology Manager, Polymers, TENNECO CHEMICALS, INC., Piscataway, NJ, USA.

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PVC AND ITS USES

I. POLYMERS: ENERGY ASPECTS

Vinyl

Vinyl is a term applied to a family of plastic products made from a polymer called polyvinyl chloride. Common polymers include such naturally occurring materials as wood, wool, and cotton; and man-made materials such as nylon, rayon, and polyethylene. Vinyls are noted for their versatility; they may be rigid or flexible, transparent or opaque.

Polyvinyl chloride (PVC) was discovered over 100 years ago but did not achieve commercial significance until the 1930's. Today it is one of the most widely used plastic materials in the world. It is used in such diverse applications as flexible coated fabrics, insulation for wire and cable, potable water pipes with 50-year strength ratings, flexible food wrap, siding for homes, and flooring.

Polymer Selection

The selection of which polymer to make or use is determined by the properties required by the end product and the economics of its use. Slide 1 shows some of the considerations that must be made.

General Polymer Properties to be Considered

Hardness

Softening Temperature

Tensile Strength

Impact Resistance

Aging Characteristics, Heat, Light, Moisture

Process Ability

Safety, Toxicity

Clarity

Ability to Modify and Formulate

Flammability

Conductivity; Electrical, Heat, Cold

Cost

Energy Considerations

Let's focus for a moment also on energy considerations. Slide 2 (Offshore Drilling Rig). While the world seems to have a better balance of oil and gas production and consumption currently than appeared likely a few years ago, nevertheless it is cost and a big gamble when drilling for oil. Therefore, we must use our oil wisely. When oil is used as fuel for cars, it is gone. When oil is used to make polymers and plastics, many people are employed, useful articles are produced, and the energy can still be recovered by burning the plastics as fuel when their useful life is complete.

Slide 3 shows that in the U. S., where much plastic is produced, that only a small percentage of each barrel of oil is used to make the plastics.

Use of Oil & Gas for Plastics

From Each Barrel of Oil:

31.3% is used for transportation

23.3% is used for heating

24.0% is used for industrial

11.3% is used for electric utilities

10.1% is used for non-energy uses

1.5% (from non-energy uses) is used as feedstocks for plastics.

Most plastics use less energy in their manufacture than many of the materials they can replace. PVC has one advantage over most plastics in that 57% of the molecule is made up of chlorine. The chlorine is derived from salt, which is plentiful, although it takes a source of energy to make the electricity for electrolysis of salt to make chlorine and caustic. Slide 4 compares energy requirements of some common materials.

Energy Requirements of Plastics and Competitive Materials

| <u>MATERIAL</u> | <u>THOUSAND BTU/CU. IN.</u> |
|---------------------------|-----------------------------|
| <u>Plastics</u> | |
| Nylon | 3.7 - 3.9 |
| Polyester | 3.2 |
| Polycarbonates & Acrylics | 2.8 |
| Polypropylene | 2.4 |
| Polyvinyl Chloride | 1.8 |
| Polystyrene | 1.6 |
| High Density Polyethylene | 1.4 |
| Low Density Polyethylene | 1.1 |
| <u>Other</u> | |
| Magnesium | 8.2 |
| Aluminum (Die Cast) | 7.8 |
| Zinc (Die Cast) | 5.8 |
| Steel | 5.5 |

II. VINYL CHLORIDE MONOMER MANUFACTURE

Polyvinyl chloride is produced by the polymerization of the monomer vinyl chloride. Vinyl chloride monomer (VCM) is produced by combining chlorine plus ethylene. Slide 5 shows the three principle methods that have been used to manufacture vinyl chloride.

VCM Manufacture

A. Acetylene + H Cl \rightarrow Vinyl Chloride

Process Largely Obsolete

B. Ethylene + Chlorine \rightarrow EDC

EDC \longrightarrow Vinyl Chloride + H Cl

Cracking furnace

C. Oxychlorination

Ethylene) Combined Chlorination

Chlorine) and Oxychlorination \rightarrow Vinyl Chloride

Oxygen) Chloride

The acetylene route is a simple process but is largely obsolete because of the high cost of manufacturing the acetylene. The oxychlorination route is used in most current VCM plants. Both Stauffer and B. F. Goodrich have well known processes which are licensed for making VCM. Current new plants in the U. S. are sized in the 1 billion lb./year size.

Vinyl chloride monomer is a gas at room temperatures. It forms explosive mixtures over a wide range of concentrations in air so precautions must be taken to avoid fire and explosion. It is stored and handled by being compressed to a liquid state. Boiling point of vinyl chloride at atmospheric pressure is minus 13°C. It is

necessary to keep monomer purity high to insure reproducible quality polymerization.
Slide 6 gives typical monomer specifications.

Specifications for Vinyl Chloride Monomer

| <u>Analysis</u> | <u>Limit</u> |
|------------------|--------------------------------------|
| Acetaldehyde | 5 p.p.m. max. wt. |
| Acetylene | 1.0 p.p.m. max. wt. |
| Acidity (as HCl) | 1 p.p.m. max. wt. |
| Appearance | Clear and free from suspended matter |
| Butadiene | 9 p.p.m. max. vol. |
| Color | Colorless |
| Inhibitor | None |
| Iron | 0.5 p.p.m. wt. |
| Methyl Chloride | 100 p.p.m. max. wt. |
| Nonvolatiles | 100 p.p.m. max. wt. |
| Peroxides | 0.1 p.p.m. max. wt. |
| Purity | 99.9% wt. min. |
| Sulfur | 1.0 p.p.m. max. wt. |
| Water | 100 p.p.m. max. wt. |

As you can see, this typical commercial specification calls for high purity monomer. This is necessary to insure reproducible kinetics, freedom from gels, and good heat stability.

III. POLYMERIZATION PROCESSES

Slide 7 shows the commonly used methods of PVC manufacture.

Methods of PVC Manufacture

SUSPENSION: H_2O + Susp. Agent and VCM + Initiator
Plus Agitation = Slurry,
Centrifuge + Dry

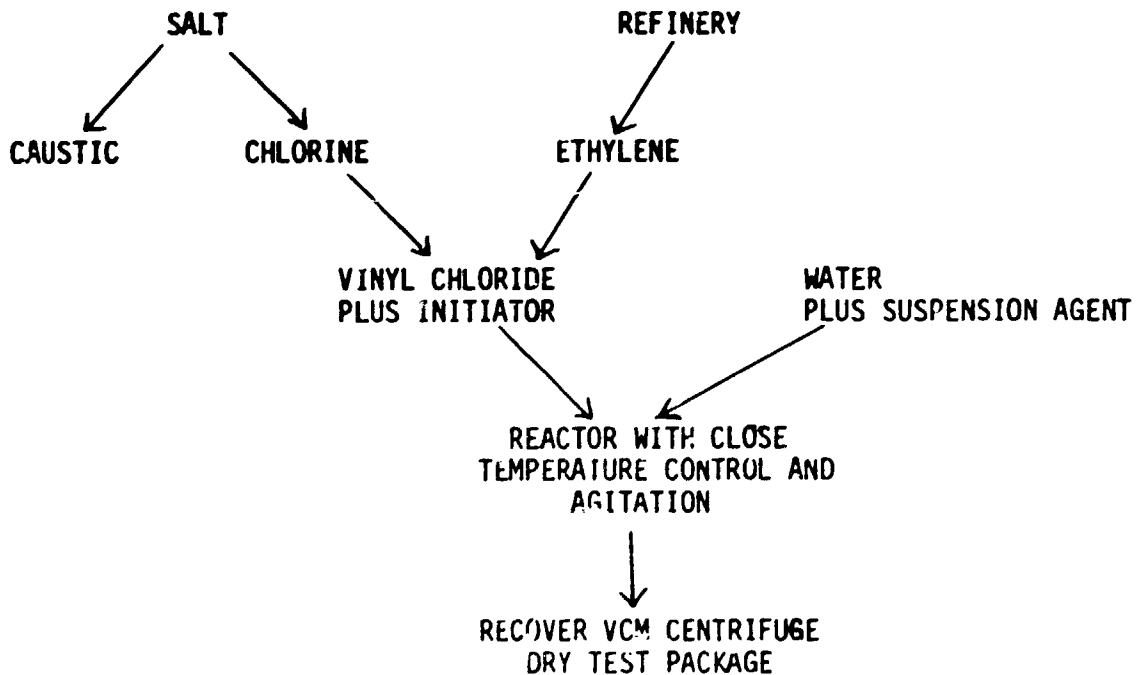
EMULSION: H_2O + Emulsifier + Initiator and VCM
W/Mild Agitation = Latex, Spray Dry

MASS POLYMER: VCM + Initiator and Rigorous Agitation + Polymer

SOLN POLYMER: VCM + Solvent for VCM. As Polymer Forms, it
Precipitates, Evaporate Solvent

Suspension polymerization is by far the most widely used method for production of PVC. The granular product is relatively easy to separate, can be made in a range of molecular weights, is relatively pure, and offers good economics. Slide 8 is a schematic of method of suspension PVC polymerization.

PVC Manufacture Suspension System



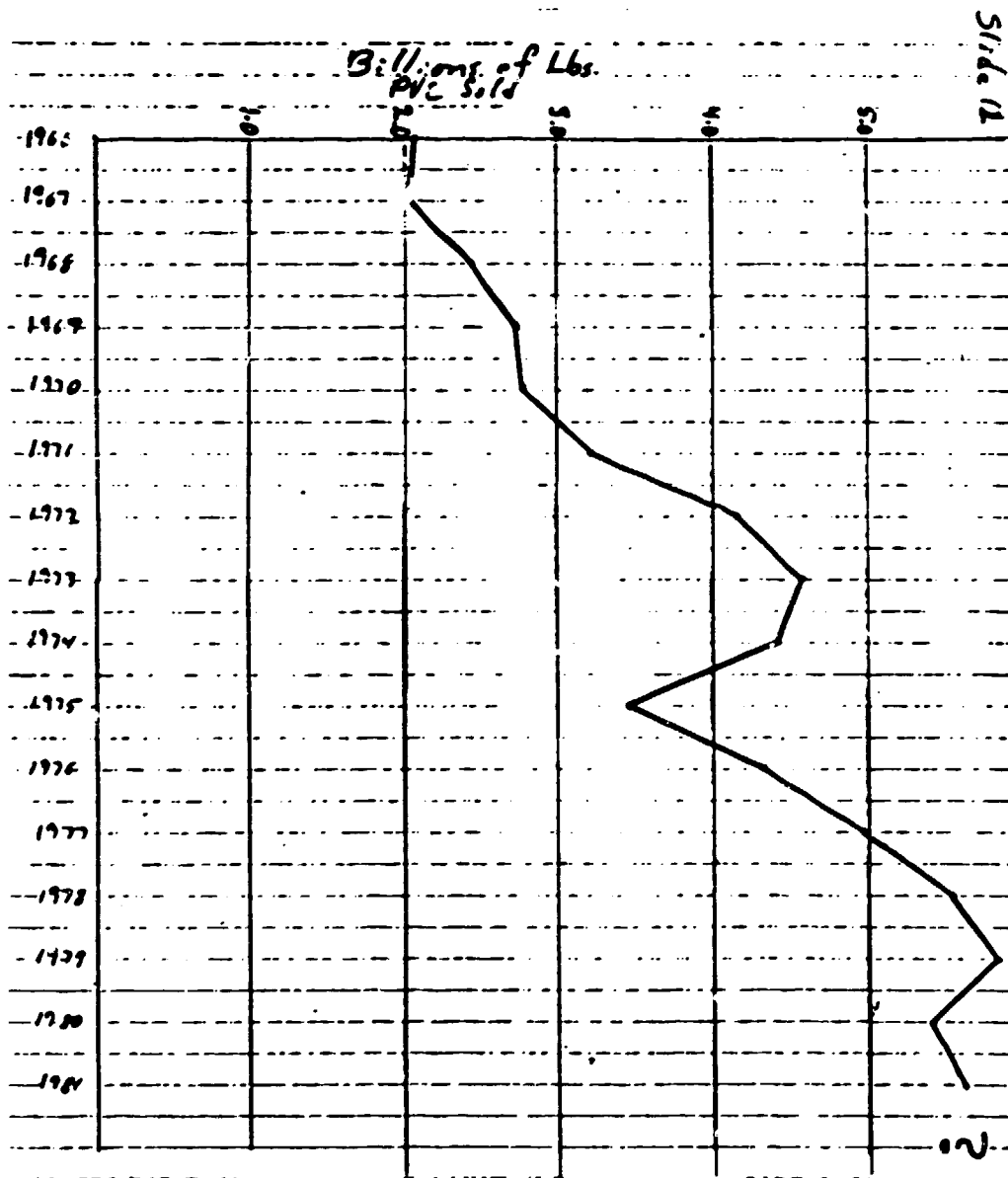
Production of dispersion resins via emulsion polymerization yields special properties but traps emulsifier, and is costlier and harder to control. Mass or bulk polymerization of PVC is harder to produce in various molecular weights but is very clean. Solution precipitation is used almost exclusively to give copolymers with narrow molecular weight range for use in solvent coatings. In all processes, an initiator such as a peroxide is decomposed by heat to yield two free radicals, each of which can initiate a rapid addition of VCM to form a polymer molecule. Temperature is closely controlled to control rate of initiator breakdown, hence to control molecular weight. Reaction is very exothermic, so temperature must be carefully controlled.

There is a definite pattern to make capacity expansions utilizing large reactor technology. We expect this trend to continue. For instance, my company, Tenneco Chemicals, uses large reactor technology licensed from Shin-Etsu of Japan in our modern plant in Texas. We understand that Huls in Germany uses 50,000-gallon reactors (190 cu. meters). Small reactors are simply not as economical, and for the same capacity there are so many more places for losses of PVC and polymer. Many small reactor plants are being dismantled. Slide 9 (Pasadena PVC Plant) gives an aerial view of our plant. Since you cannot afford to make mistakes in a 35,000-gallon (133 cu. meter) reactor, this plant is highly automated with a computer center functioning to control much of the operation. Slide 10 shows a portion of the computerized control room at Pasadena.

Slide 11 is a picture of a typical suspension PVC particle. Diameter of the particle is about 150 microns. Note the porosity of the particle. Each particle is really made up of primary particles. The porosity helps in blending and compounding and in the aesthetics of end products produced.

IV. PVC MARKETS

The PVC markets are quite cyclical in nature, rising with the automotive, and especially the construction, markets and growing overall. We are currently in a recessionary mode. This brings low prices, but this also makes for better penetration against competitive materials. Slide 12 plots U. S. sales of PVC from 1966 - 1981.



Slide 13 lists the current largest producers of PVC in the U. S. Much of this is located near the Gulf of Mexico, where ethylene and energy are more available. PVC is normally converted close to the monomer plants so that VCM does not have to be shipped long distances.

PVC CAPACITY, MAJOR SUPPLIERS

Millions of lbs.

1982

| | |
|---------------------|--------------|
| B. F. Goodrich | 1,500 |
| Tenneco | 1,000 |
| Hooker | 900 |
| Shintech | 700 |
| G - P | 700 |
| Concco | 600 |
| Borden ¹ | 500 |
| | <hr/> |
| | <u>5,900</u> |
| Others ² | <u>2,500</u> |

¹Adding in 1983

²Includes Formosa adding in 1982.

Slide 14 gives the 1981 usage of PVC in the U. S. according to statistics tabulated by the Society of the Plastics Industry. Note that PVC pipe is by far the largest user of PVC.

1981 PVC USAGE - M LBS.

(Modern Plastics)

| | | |
|----------------------------|-------|--------------------|
| Extrusion Total | | <u>3,240</u> |
| Extrusion Pipe | 2,032 | |
| Extrusion Wire & Cable | 374 | |
| Extrusion Packaging | 308 | |
| Extrusion Siding | 180 | |
| Calendering Total | | <u>812</u> |
| Calendering Flooring | 150 | |
| Calendering Packaging | 79 | |
| Calendering Upholstery | 75 | |
| Calendering Automotive | 70 | |
| Injection Molding | | <u>323</u> |
| Injection Molding Fittings | 110 | |
| Phono Records | | <u>108</u> |
| Blow Molding | | <u>99</u> |
| Dispersion Coating | | <u>306</u> |
| Dispersion Molding | | <u>185</u> |
| Solution Coating | | <u>55</u> |
| Latex | | <u>55</u> |
| Export | | <u>429</u> |
| | | <hr/> <u>5,612</u> |

PVC is treated like a commodity plastic, but it really is not. Many grades exist. Many individual cuts or grades are needed for specific end product uses. Uniformity of each grade is a must. Careful quality control must be performed on each grade. Slide 15 shows typical properties tested on a grade of PVC used primarily for wire and cable coating--PVC 250-3.

Key Properties of PVC 250-3

| <u>Property</u> | <u>Expected Range</u> |
|--|-----------------------|
| 1. Relative Viscosity, 1% solution by wt. in cyclohexanone at 25°C | 2.45 - 2.51 |
| 2. Dry blend time | 6.5 min. max. |
| 3. Cleanliness grade, really a summation of visual contamination, magnetic, total gels, and large gels | general purpose |
| 4. Volatiles | 0.4 max. |
| 5. V. R. (Ohms/cm. ² x 10 ¹²) | 10 minimum |
| 6. Loose bulk density, lbs./cu. ft. | 29 - 33 |
| 7. RVCM | 10 p.p.m. max. |
| 8. Screen analysis | |
| retain on 40 mesh | nil |
| retain on 60 mesh | 3% max. |
| pass thru 140 mesh | 20% max. |
| pass thru 200 mesh | 2% max. |

V. PVC TESTING

Molecular Weight is normally determined by means of a dilute solution viscosity. The effect of a solution of the resin on the viscosity of a solvent used is a predictor for molecular weight differences. Most common test is inherent viscosity using ASTM-D1243 procedure. Small melt mixers such as a Plasti-Corder can also be used to measure torque required to melt mix resin or compound. Slide 16 (Prabender Plasti-Corder) and Slide 17 (Plastigraph Showing Torque).

Gels or Fisheyes PVC is mixed with plasticizer and carbon black and milled under controlled conditions on a heated two roll mill. Hard particles do not masticate well so show up as an imperfection when film is viewed against a light. Slides 18 and 19 (Two Roll Mill Operation).

Plasticizer Sorption In this test a plasticized mix is stirred with a Sigma blade mixer on a Plasti-Corder at a moderate temperature, such as 80°C, and the transition from wet mix to a dry mix where plasticizer is absorbed into the resin is measured.

Particle Size Measured by screening through progressively finer screens on a ro-tap shaker.

Contamination Best observed by use of a Syntron Vibrator but can be done visually by hand.

RVC Determined by the resin producer using gas chromatography.

Bulk Density Measure weight of resin in a 100 ml. cylinder.

Volatiles Measure weight loss of the PVC after 30 minutes in a circulating oven at 105°C.

VI. COPOLYMERS

A small but important segment of the PVC industry is the production of copolymer. The most common copolymer is made with vinyl chloride content at about 85% and vinyl acetate content 15%. Slide 20 shows the primary advantages and disadvantages in the use of copolymers.

Copolymers: Vinyl Chloride--Vinyl Acetate

Advantages

1. Easy processing.
2. Low energy requirement.
3. High binding power.

Disadvantages

1. Poor heat stability.
2. Low HDT.
3. Poorer physical properties.

Primary uses for copolymers are in the manufacture of flooring, phonograph records, solution resins and films. Slide 21 gives an approximate breakdown of markets for copolymer.

U.S. Copolymer Resin Use--1981

(Millions of Lbs.)

(Tenneco Estimates)

| | |
|--------------------|-----------|
| Flooring | 120 |
| Phonograph Records | 120 |
| Solution Resins | 100 |
| Rigid Film | 30 |
| Export | 10 |
| Copolymer Latex | 30 |
| Blending Resin | 8 |
| All Others | <u>13</u> |
| TOTAL: | 431 |

Vinyl chloride can be copolymerized with other monomers besides vinyl acetate but to date they are of little commercial significance.

VII. DISPERSION RESIN

Since a plastisol is a dispersion of fine particle size emulsion polymer in plasticizer, we are concerned about its viscosity, sometimes at low shear and sometimes at high shear. The common tests to determine this are the Brookfield for low shear viscosity determination and the Severs for high shear. A simple analogy is that molasses would have a high Severs and low Brookfield, and mayonnaise would be vice versa. It is also desirable to know viscosity characteristics after storage of various periods of time--for example, one day and one week.

Since plastisols or organisol are often used for thin coatings, you do not want streaking to occur. The measurement of coarse particles is best done by making a drawdown of the paste on a tapered depth bar to see how thin you can drawdown without getting streaks.

VIII. PVC ADDITIVES

PVC is a remarkable plastic because it can be readily blended with various additives which drastically change its properties. Straight PVC is a hard horny material with poor heat stability and processing. Plasticizers can be added to soften PVC; stabilizers are necessary to protect the polymer during processing; lubricants are added to assist processing; and modifiers may be added to change impact and processing. In addition, fillers and pigments can be added over a wide range.

Plasticizers for PVC

Most plasticizers for PVC are high boiling esters. The most commonly used is di 2 ethyl hexyl phthalate, commonly called dioctyl phthalate or DOP. DOP has had nearly 50 percent of the market, but the 2 ethyl hexyl alcohol has been in worldwide short supply, so people are using alternates, mostly linear phthalates. Phthalates account for about 80 percent of all plasticizers used. Plasticizers may be added in amounts up to 100 parts per hundred of resin (100 p.h.r.) for very flexible applications. (Note: most PVC technologists refer to p.h.r. addition of additives, not percent of total composition.)

If superior low temperature properties are required, plasticizers such as sebacates and adipates are commonly used.

If more permanance is required, it is common to use higher phthalates such as di tri decyl phthalate. Tri mellitate types are also used in high performance electrical applications. For maximum permanence, polymeric plasticizers may be selected, though usually at a sacrifice in plasticizing efficiency, and in cost.

STABILIZERS

Stabilizers are added to PVC to prevent adverse degradation of the polymer during processing and to a lesser extent in end products. The primary chemical functions of the stabilizer should be:

- A Act as H Cl scavengers
- B Eliminate labile sites which initiate dehydrochlorination
- C Modify polyene structures and retard color color uevelopment, chain scission and cross linking
- D React with free radicals as formed
- E Act as anti oxidants

The most commonly used materials used as stabilizers for PVC are listed below:

Ba-Cd or Ba-Cd-Zn mostly used in flexibles
Sn mostly used in rigids
Pb used in flexible and in rigid
Ca-Zn used in food packaging applications
Phosphites used as costabilizers in flexibles
Epoxidized oils used as costabilizers

Lubricants

Lubricants are considered to have two functions according to their structure and utility in the PVC.

Internal lubricants such as Ca stearate assist in fusion of the compound and are reported to help in polymer chain movement and plasticity in the molten state.

External lubricants such as waxes are thought to function primarily by preventing the molten polymer compound from sticking to processing equipment surfaces.

As you will see later, it is common to use a mixture of internal and external lubricants, especially in rigid PVC processing.

Modifiers

Here we are talking about polymeric process aids and about impact modifiers.

Process aids function by (1) aiding in fusion of the compounds and (2) by enhancing the hot melt strength of the hot melt. Most commonly used type is a fine particle size acrylic powder at levels of 1 to 3 phr.

Impact modifiers are polymeric materials that introduce little rubbery particles that intercept and cushion growing cracks in the plastic to keep them from propagating. Commonly used types are ABS and MBS, where the rubbery butadiene effects the impact improvement. Also used are acrylic types where a soft component such as butyl acrylate does the work. Another is chlorinated polyethylene which is more rubbery than PVC.

IX. Mixing and Compounding

Blending of PVC compounds is done with either an intensive mixer where the dry blend is then used to feed the processing equipment, or the compound may be mixed on a simpler mixer such as a ribbon blender and then hot melt mixed on a Banbury, Continuous Hot Melt Mixer or an extruder--pelletizer. The intensive mixer is the simplest and cheapest but does not give any melt homogenization prior to processing. Product from a Banbury or Continuous Melt Mixer is often dropped on to two roll mills which sheet out the hot melt for dicing into granular product.

Slide 22 shows an intensive mixer. As the intensive mixer puts lots of energy into the compound, it gets warm, so is normally dropped into a cooling mixer in tandem, which is nothing more than a jacketed low intensity mixer with cool water moving through the jacket.

Slide 23 and 24 shows a small extruder pelletizer for face cutting of pellets. Compound can also be kneaded on a Continuous Mixer that feeds a mill and dicer. Tenneco has two such units each of which can produce about 9,000 lbs./hr.

X. Rigid PVC in Construction

Rigid PVC processing developed rapidly in Europe following the Second World War because they were short of traditional construction products and properly formulated rigid PVC has excellent properties for many construction products. Today rigid PVC is the dominant growth area for PVC worldwide. Slide 25 shows the advantages and disadvantages of rigid PVC in construction.

PVC - Advantages in Construction

1. Hard
2. Abrasion Resistant
3. Permanence
4. Color Throughout
5. High Rigidity, Strength
6. Low Conductivity, Electricity and Heat
7. Low Flame Spread
8. Rot and Corrosion Resistant
9. Can Be Readily Formulated
10. Reasonable Cost

PVC - Disadvantages in Construction

1. Limited Flexural Modulus
2. Limited HDT

There has been much controversy over the use of single screw extruders vs. twin or multi screw extruders. In general, twin screw extruders cost more and maintenance is higher but savings can be made in formulation because the twin screw extruder is like a positive pump and its performance is not formulation sensitive and temperature of the melt can be better controlled. A single screw extruder depends on friction of the melt with the barrel to develop mixing and higher temperatures are generally used. In many instances singles are used for extrusion from pelletized compound and twins are used for extrusion of dry blend.

XI. PVC Pipe

PVC Pipe is now manufactured in diameter up to 27 inches, (68 cm), in the U.S. Most is extruded from powder blend on twin screw extruders. A typical formula is given in Slide 26.

Typical PVC Pipe Formula

| | |
|--------|----------------------------|
| 100. | PVC (I.V. of .92) |
| 0.4 | Sn Stabilizer |
| 0.6 | Ca Stearate |
| 1.2 | Wax 165 |
| .15 | AC 629A |
| 1.0 | TiO ₂ |
| 3.0 | Treated Ca CO ₃ |
| <hr/> | |
| 106.35 | |

A breakdown of the estimated markets for PVC pipe in the U.S. in 1981 is given in Slide 27.

U.S. PVC Pipe Shipments - 1981

(millions of lbs.)

| | |
|-----------------------------|-------|
| Pressure - H ₂ O | 779 |
| Irrigation | 224 |
| Conduit | 370 |
| Sewer & Drain | 310 |
| Drain, Waste, & Vent | 229 |
| Gas Pipe | 22 |
| Other | 79 |
| <hr/> | |
| | 2,033 |
| Pipe Fittings | 110 |

One of the reasons the pipe industry has grown rapidly and is now the biggest single outlet for PVC is that very high standards of performance, especially high hydrostatic design stress, were established early. Pipe is designed to have a high HDS even after 50 years service. The next series of slides gives you a picture of some PVC pipe operations.

- Slide 28 Pipe extrusion
- Slide 29 Pipe puller and saw
- Slide 30 Belling of pipe
- Slide 31 Belled pipe
- Slide 32 Finished pipe bundle
- Slide 33 Pipe storage yard

An interesting segment of the irrigation market is rapid growth of "drip irrigation systems" using small diameter polyethylene or PVC with tiny emitters that regularly release small amounts of water to growing plants. Since these are buried, they avoid huge losses of water normally incurred in ditch and other surface irrigation. It is normally employed in specialized orchard crops where economics allow the farmer to cover the added cost and cultivation does not disrupt the system.

XII.

Injection Molding

In DWV installation, there are a large number of fittings required to accommodate bends, traps, joints, etc. PVC fittings are made by screw injection molding. In order to get good flow properties, injection molding compounds are normally made with lower molecular weight resin. This sacrifices physicals, so impact modifiers are used. Because of the high heat and high shear generation stabilizer levels are high. Slide 34 gives a typical formulation.

Formulation Rigid Injection Molding

| | |
|------|---------------------|
| 100. | PVC (I.V. of .74) |
| 1.5 | Acrylic Process Aid |
| 5. | MBS Impact Modifier |
| 2. | TiO ₂ |
| .9 | Ca Stearate |
| 1.3 | Wax 165 |
| .15 | AC 629A |
| 2.0 | Sn Stabilizer |

XIII. Vinyl Siding

Vinyl Siding (If Properly Formulated) has a number of advantages as shown on slide 35.

PVC in Vinyl Siding

Advantages

1. Does not Dent
2. Color Throughout
3. Good Weatherability
4. Cheaper than Aluminum
5. Attractive Surface
6. Not an Electrical Conductor

Disadvantages

1. High Thermal Expansion
2. Not Suitable in Dark Colors

It would not be good enough for exterior applications if it was not loaded up with titanium dioxide to screen the PVC from ultra violet light. A typical formulation is given in Slide 36.

Siding Formulation

| | |
|------|-------------------------|
| 100. | PVC (I.V. .94 - .96) |
| 7. | Acrylic Impact Modifier |
| 2. | Acrylic Process Aid |
| 2. | Tin Stabilizer |
| 0.8 | Ca Stearate |
| 1.0 | Max 165 |
| 0.15 | AC 629A |
| 14. | TiO ₂ |

126.95

There have been many attempts to develop adequate accelerated weathering tests to predict exterior durability. Unfortunately, that work has not correlated well with actual exposure results. It is current industry practice to expose extrusions at a 45 degree angle South in Arizona (a hot dry climate); in Florida, (a hot humid climate); and in a Northern U.S. industrial climate. Color and impact retention is most difficult to achieve in Arizona. The 45^o So. exposure is known to be worse than verticle. A minimal change in two years in Arizona is the target. At the same time, 15-20 year actual home exposures have stood up well with early siding formulations. It is important that accessories, corners, fascia, soffits, etc., be made from the same quality material. Normally, either PVC or aluminum siding is installed over about 1.5 inch polystyrene foam backer board for insulation purposes. Slide 37 shows an attractive home finished in vinyl siding.

XIV.

Window Profiles

PVC window frames have made big penetration into the window market in Europe. PVC is an excellent choice of product for this application because it does not warp, swell, or shrink. It does not need painting and it is a very poor conductor of heat. It will undoubtedly replace aluminum frames which have been widely used.

The Anderson Corporation in the U.S. makes a vinyl over wood window frames that has good public acceptance. See Slide 38. Slide 39 shows some different profiles made in Europe and in the U.S. Note one of the European extrusions has a darker color co-extruded. We also have seen co-extrusion where the flexible seal to the glass is co-extruded on the rigid. For optimum insulation value the glass used is usually a double layer with the air space between acting as insulator.

The range of profiles is almost unlimited. Slide 40 shows a PVC rain gutter for a home.

In both vinyl siding and in vinyl window frames, committees are working within ASTM to set appropriate standards to help insure that only quality products get to the marketplace.

XV.

Rigid Clear PVC Blow Molding

Rigid PVC is also used to make PVC bottles. Bottles are used for shampoos and other cosmetic uses and also for food packaging applications - but not for packaging alcoholic beverages. Most blow molding is done by free extrusion and clamping and blowing to the shape of the mold. Some small bottles are made by injection blow molding. 99 million pounds of PVC were used for PVC bottles in 1981. A typical formulation is given below in Slide 41.

Formulation, PVC Bottles

| | |
|-------|---------------------|
| 100. | PVC (I.V. of .66) |
| 15. | MBS Impact Modifier |
| 2.5 | Acrylic Process Aid |
| 2.5 | Sn Stabilizer |
| 0.4 | Hostawax E |
| 1.0 | GMS |
| 0.1 | PE Wax |
| --- | Toner |
| <hr/> | |
| 121.5 | |

Rigid Sheet

Rigid clear film and sheet made for blister packs. etc. would be made by calendaring or extruding a similar formulation, but probably lower in impact modifier and stabilizer. Sheet for credit card stock may be made with high molecular weight copolymer.

XVI. Flexible PVC

At least in the U.S. the flexible markets are more mature and more closely aligned to population growth and overall economic changes. Lets take a look at some of these areas.

Film

While some film is processed by extrusion, the majority is manufactured by calendaring. Calendars are really large two roll mills with two or three additional rolls to meter a precise amount of thickness of molten plastic to the final rolls. They are often fed by a system including a blender and a continuous hot melt mixer. A large calender has a high initial cost, but it is an economical means of producing a large quantity of film or sheet at a high rate. Films can be produced in a wide range of thickness and from completely rigid to highly plasticized.

Slides 42 and 43 show a swimming pool liner and a boat cover made of vinyl film and vinyl laminated to fabric.

PVC Meat Wrap

Another important and growing market for PVC is in clear thin flexible meat wrap. This type package lets the consumer view the meat products while still protecting them and limiting the vapor transmission - especially oxygen transmission. Film is made by blown film extrusion technique. A typical formula is given in Slide 44.

Meat Wrap Film

| | |
|------|-----------------------------|
| 100. | Medium molecular weight PVC |
| 25. | Di 2 ethyl hexyl phthalate |
| 15. | |
| 3. | Epoxidized soya oil |
| 1. | Ca-Zn phosphite stabilizer |
| 0.5 | Stearic acid |

Some of the major end products include flooring such as vinyl asbestos tile and film laminated to fabric for automotive or upholstery applications. Rigid films are calendared for use in blister packs, credit cards, and a wide range of packaging applications.

Wire and Cable

Insulation of electrical wire and cable is another large and important use of PVC. It is estimated that 374 million pounds of PVC was used for wire and cable in 1981. Wire and cable compounds are plasticized with a wide range of plasticizers according to the end product specification. For instance, DOP may be used for 60⁰ wire, DIDP for 75⁰ wire and trimellitates for 105⁰ performance wire. Lead stabilizers are normally used because of good electrical properties, (poor conductors of electricity). Clays are

used as fillers instead of calcium carbonates - again because of better electrical properties. Cross head extrusion is used. The wire crosses the front of the extruder. Some machines are capable of speeds as high as 4,000 ft./minute. Key markets for PVC in coated wire and cable are given in Slide 45.

PVC Electrical End Uses

| | <u>Percent</u> |
|---|----------------|
| Building Wire | 55 |
| Communications Wire | 15 |
| Flexible Cord (Extension cords, Household Lamps) | 15 |
| Automotive Uses | 10 |
| Appliance Wire | 5 |
| | <hr/> |
| | 100 |

Medical Products

PVC can be used to fabricate many useful articles used in the medical field. Two of the most common are blood bags and intravenous tubing. Because the film used for blood bags is clear and because it is collapsible, it makes an ideal holder for the blood. PVC's flexibility and low cost make it ideal for intravenous tubing. Formulating for medical applications is quite simple since the end product is clear. TQP is sanctioned by FDA for this use. Calcium-zinc stabilizers are used along with a few phr of epoxidized soy bean oil as costabilizer.

XVII.

Coating Resins, Systems

There are four basic types of PVC coating: plastisol/organisol, solutions of copolymers, latex and powder coating.

Dispersion and Blending Resins

The largest of these is the plastisol/organisol market - commonly called the dispersion market. Dispersion resins are very small particle size resins (generally less than 5 microns) of high molecular weight, with a fairly high amount of residual emulsifier. They can be mixed with plasticizer to make a fluid plastisol or paste. Sometimes less plasticizer is desired so a non-solvating organic diluent such as naphtha is added. This is called an organisol. These dispersions can be used for dipping (gloves or tool handles), spreading on fabrics, coating on substrates for flooring, etc. The liquid coatings are cured with heat. Foamed flexible coatings are easily accomplished by incorporating chemical blowing agents. Control of dispersion rheology is extremely important.

Markets for dispersion resin in the U.S. are shown in Slide 48. The blending resins referred to are very fine particle size suspension resins used as lower cost extender resins in applications where their larger particle size can be tolerated. Slide 46.

U.S. Dispersion Resin Use - 1981

millions of lbs.

(Tenneco Estimate)

| | <u>Dispersion</u> | <u>Blending</u> |
|-----------------------------------|-------------------|-----------------|
| Protective Coatings, Adhesives | 140 | 7 |
| Flooring | 90 | 30 |
| Textile | 56 | 15 |
| Formulating, Molding, & All Other | 160 | 30 |
| | <hr/> 446 | <hr/> 82 |

While dispersion resins are more costly to make, they can be used in a wide range of products and many of the special applications are not capital intensive. One of the large uses is in flooring. The next three slides show some flooring applications.

Slide 47 Cross section of foamed flooring

Slide 48 Installed vinyl flooring

Slide 49 Installed vinyl flooring

Solution

Solution copolymers are primarily those produced by solution precipitation where the control of molecular weight is very good. End applications include can coating, marine and industrial paints, and as components of a wide range of enamel and special paint.

Latex

Vinyl chloride polymerized in water emulsion that has not been dried can be used as a PVC latex. It is not film forming at room temperature, but can be made so by proper addition of plasticizer and/or heat.

Powder Coating

PVC powder coatings are a relatively small market. Formulated dry blend can be fluidized with air and applied to hot metal parts by dipping the metal in the fluidized bed or by electrostatic spraying.

XVIII.

Copolymer. Phonograph Records

Earlier we had listed the major markets for copolymer. The production of phonograph records is a large consumer of PVC with 108 million pounds used for this application in 1979 in the U.S. The primary resin used is a copolymer with an inherent viscosity of about 0.50 and a bound vinyl acetate content of about 13-15%. This is often modified with addition of about 10% of a secondary resin that may be a low molecular weight homopolymer or a low acetate copolymer. This is added to modify the rheology of the hot melt. The polymer is poured

quickly and cooled in the press (as low as 18 second total cycle time) and must conform to each and every groove and to every sound vibration in each groove. Records are really made by compression molding of a hot melt. A typical formulation is given in Slide 50.

Typical Phonograph Record Formulation

| | |
|--------------------------------|-----|
| 13% Acetate Copolymer | 90. |
| Low Acetate Copolymer | 10. |
| Lead or Barium Lead Stabilizer | 1. |
| Carbon Black | 0.5 |
| Calcium Stearate | 0.3 |

All ingredients must be free of contamination that would cause extraneous sound in the record. Quality control on the materials, compounding, and final record is important. Slide 51 shows equipment used in testing the record.

XIX.

Safety and Health

Since vinyl chloride monomer boils at minus 13°C, it was a big surprise to find residual VCM in PVC that had been dried at relatively high temperatures and then processed at high temperatures. Nevertheless, it was determined that PVC did retain some VCM that could then migrate into such items as cooking oil or alcoholic beverages packages in PVC bottles. At the same time, it was found that a few workers in PVC plants that had been exposed to large quantities of VCM over a long period of time had developed an unusual type of liver cancer called angiosarcoma. Industry was called on to better contain VCM in their plants and to sharply reduce residual VCM in PVC. This has been done.

Slide 52 sums up the key regulations employed in the U.S. to control VCM exposure.

Key Regulations Affecting PVC

1. OSHA 1PPM max. TWA in worker area
2. EPA Limits emissions in all polysteps to 10PPM max., slurries to 400PPM and 2,000PPM
3. TOSCA All products on file; new chemicals need testing, pre-registration, and approval
4. FDA September 3, 1975 proposal not acted on, current indecision

The OSHA regulation was intended to protect workers in VCM-PVC plants but also in fabricated plants. The PVC producers have done such a good job of reducing residual VCM that fabricators have not been reaching action levels in their plants. The EPA ruling has had a major effect on how PVC producers handle and strip their resins. Both have caused expenditure of large amounts of money for compliance, but the workplace is undoubtedly safer than before the days of industry becoming aware of the potential problem.

The FDA situation is so unclear that we hesitate to comment on it. At the present time, PVC can be used in food packaging applications and potable water pipe but not in bottles for alcoholic beverages. An expected new ruling will undoubtedly include very low limits on residual VCM in PVC food packaging films, bottles, medical tubing, etc. The level might be as low as 1-2 parts per billion. No one knows at this time.

The Society of the Plastics Industry in New York City is a valuable source of information on regulations concerning plastics and has a wide range of generic information on plastics applications and uses. Ask for their bulletin on SPI literature.

XX. Alternate Polymers

If PVC is such a miraculous polymer, why not use it exclusively? There may be many reasons. To achieve commercial significance and long life, a product must have good cost performance. We urge you to compare cost performance of products made with alternate materials against PVC. You will find PVC winning more than its share of those comparisons. Slide 53 shows some of the materials that compete with PVC in various areas.

Competitive Materials

Application

| | |
|--------------------|---------------------------|
| Pipe | Polyethylene, Fiberglass |
| Wire & Cable | Polyolefins, Polyurethane |
| Packaging | Polyolefins, EVA |
| Siding | Kovel, Noryl |
| Blow Molding | PET, Polypropylene |
| Dispersion Coating | Polyurethane, Epoxy |

XXI. Futures, Growth Areas

While PVC will have some ups and downs according to overall economic strength - particularly construction markets, it will nevertheless continue to grow. This is especially true for rigid PVC. Much of this growth will come at the expense of traditional products such as steel, wood, copper, and aluminum.

Slide 54 shows some of the areas that I think will show considerable growth for PVC.

Growth Areas

Windows

Aluminum Replacement

Injection Molding

Decorative Fencing

Construction Products in General

Medical Products

XXII.

Conclusions

PVC is a remarkably versatile polymer with good economics. It can be fabricated into a wide range of useful products. It is a good way to utilize our energy resources. The biggest growth will be in the use of rigid PVC for construction products.

We wish to thank UNIDO for giving me the opportunity to speak to you about PVC. We welcome your questions and will be available for your consultation and help.

