HI-FAX POTENTIALS IN THE WIRE AND CABLE INDUSTRY

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Before starting our discussion in reference to these new Hi-fax polymers, we would like to indicate that this should be considered a progress report rather than a complete and finished item. As you all know, these linear polyethylene polymers have only recently come on the market. Much work will be necessary before comprehensive knowledge of processing and use characteristics will be available on the products prepared by the Hi-fax process.

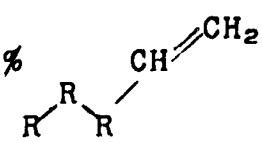
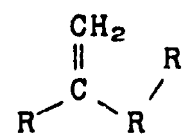
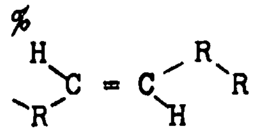
Hi-fax is a linear ethylene polymer, made by low-pressure polymerization using Ziegler-type catalysts in a process developed by Hercules Powder Company in cooperation with Farbwerke Hoechst AG. of West Germany. Compared to polyethylene made by more conventional processes which require high pressures, it can be stated that Hi-fax is more resistant to heat (35°F. higher), it is harder, stiffer, higher in tensile strength and in density, and is somewhat less affected by organic solvents and chemical reagents.

Hi-fax is essentially a paraffinic chain consisting of many hundreds of $-CH_2CH_2-$ units linked together.

It was once thought that a completely linear polyethylene would crystallize so completely that it would be too brittle for general use. It is now realized that this conclusion applies only to products of very low molecular weight, and that linear polyethylenes, as well as other polymers, of higher molecular weight, do not crystallize completely because of entangling of chains and entrapment of portions of chains between crystalline regions. In addition, the grades of Hi-fax currently offered contain short side chains, usually one for every 150 to 300 carbon atoms for the main chain. As a result of these two factors, the crystalline phase of Hi-fax, as determined by x-ray examination, comprises 75 to 80% of the total polymer. The degree of crystallinity depends somewhat on molding technique and aftertreatments. In conventional branched-chain polyethylene, the crystalline phase seldom amounts to more than 55-60%. Further infrared studies have shown that all polyethylenes contain minute amounts of unsaturation. Important characteristics of Hi-fax from the chemical and structural standpoint are summarized in Table 1.

Table 1

Typical Structural Properties of Hi-fax Polymer

Melting Point, °C.		129-132
% Crystalline		74-82
Infrared Analysis:		
Methyl groups, %	CH_3-	0.57
Vinyl groups, %		0.040
Vinylidene groups, %		0.017
Trans double bonds, %		0.03
Al*		0.01-<0.03
Ti*		0.01-<0.03

*These metal exist primarily as oxides in the polymer.

To the polymer technologist, an equally important factor is the molecular weight of the resin. A commonly accepted measure of molecular weight is intrinsic viscosity, which in essence measures the viscosity contribution of a polymer to a solution at infinite dilution. The relationship between molecular weight and viscosity depends somewhat on branching, since side chains do not contribute as much to viscosity as does the length of the main chain. The best information to date gives, for Hi-fax, the relationship between intrinsic viscosity, $[\eta]$, and weight average molecular weight, M_w, determined by light scattering:

$$[\eta] = 6.77 \times 10^{-4} (M_w)^{0.67}$$

The range of intrinsic viscosities for branched-chain polyethylenes is limited to about 0.8-1.5. Such a limitation does not exist for Hi-fax, which is now commercially available with intrinsic viscosities from 2 to 6. Some representative grades of Hi-fax, together with weight-average molecular weights calculated from the above formula are given in Table 2.

Table 2

Range of Intrinsic Viscosity	Range of Corresponding Weight-Average Molecular Weight
1.7-2.3	120,000-190,000
2.3-3.0	190,000-288,000
4.3-5.0	440,000-560,000

In the last analysis, all properties of the polymer chain, such as content of double bonds, linearity, and distribution of molecular weight, will have some influence on physical properties. Workers at our laboratories are attempting to measure these effects, and a report of some of their conclusions will appear soon. However, the fact remains that materials presently available differ primarily in linearity (measured by methyl group content) and in molecular weight.

The ability to produce linear polyethylenes with controllable and widely varying characteristics may prove to be one of the outstanding advantages of the Ziegler polymerization technique.

A great deal of thought has gone into means of classifying polyethylenes so that a common understanding can exist when reference is made to one or another type. Attempts have been made to classify by such broad descriptive terms as branched versus linear, crystalline versus noncrystalline, high pressure versus low pressure, and high density versus low density - to enumerate only a few. It is our belief, that if we classify by methyl group content (which is an indication of the degree of branching) and by M_w, that a means exists which significantly describes the product. Such a description eliminates indefinite nomenclature such as high versus low pressure, linear versus branched.

In our laboratories we have found that products prepared by the high-pressure process will vary in methyl content from 1.26% to 4.0%. The low-pressure products vary from 0.12% to 1.0% in methyl content.

On Table 3 are the differentiating characteristics of these polymers as defined by methyl group content:

Table 3

Manufacturing Process	Low Pressure	Low Pressure	Hi-fax	Low Pressure	High Pressure	High Pressure
Methyl Group, %	0.12	0.46	0.57	0.94	1.33	2.52
Rockwell Hardness	66R	53R	51R	42R	28R	-1R
Tensile Strength, lb./sq.in.	4,240	3,360	3,110	2,930	2,400	1,610
Maximum Elongation, %	300-900	ca.300	500	900	480	250
Flexural Stiffness, lb./sq.in.	117,000	116,000	99,000	112,000	6,500	3,900
Torsional Rigidity, lb./sq.in.						
at 30°C.	50,000	40,000	35,000	35,000	17,800	10,800
at 60°C.	18,700	13,400	11,800	10,700	6,200	3,100
at 90°C.	6,400	4,600	4,100	3,400	2,200	1,100
RSV.	2.1	2.3	2.5	3.0	1.5	1.2

Some indication of the relative molecular weights of the samples listed is given by the RSV, defined as the specific viscosity of a 0.1% solution in decalin at 135° divided by the polymer concentration. Most of the properties listed in Table 3 are not very dependent on molecular weight. As will be discussed later, some very important properties, such as notched impact and stress cracking do depend on molecular weight.

From Table 3 it is readily seen that although all properties do not correspond to the methyl content, it is a good means of classifying this very complex group of products. By means of the table the relative position propertywise of Hi-fax in respect to the field is readily apparent. (At the back of this report is a detailed physical property list of Hi-fax - Table 9.)

Experience has shown that as the methyl content decreases the crystallinity increases and the control of elongation becomes more difficult. It is for this reason that we have attempted to "build" into Hi-fax an optimum methyl content consistent with adequate hardness and heat resistance while maintaining pliability so that cables of acceptable flexibility can be manufactured.

Of interest also are the marked differences shown in Table 3 between products made from high- and low-pressure processes. For example, tensile strength, stiffness, and hardness.

Electrically, the new low methyl content polymers are not quite as good as the older high methyl content polymers. This is due to either crystallinity or the process by which they are prepared which leaves a small amount of ash measurable by spectrographic analysis. This ash is not catalyst because treatment of the polymer after polymerization destroys the metal halides and metal alkyls as such. The metals present are aluminum and titanium in the form of oxides. They are controlled so that in total they are below 0.06%. Because of this, however, we do not suggest at this time the use of Hi-fax in very high frequency applications. There are excellent prospects that these oxides will be further reduced so that low-methyl polyethylene will be suitable for very high frequency use. Table 4 characterizes the electrical properties of the polymer in relation to a high-pressure product.

Table 4

Electrical Properties of Polyethylenes

	A.S.T.M. Method	Hi-fax		High-Methyl Polyethylene
		Natural	Black	Black
Dielectric Constant,	D150-54T			
10^4 cps.		2.3	2.6	2.6
5×10^7 cps.		2.3	2.6	2.6
Dissipation Factor,	D150-54T			
10^4 cps.		0.0007	0.002	0.001
5×10^7 cps.		0.001	0.004	0.009
Dielectric Strength (1/8-in. disc) Short Time, v./mil	D149-44	440	-	445
Arc Resistance, seconds	D495-48T	190	65	40
Volume Resistivity, ohm-cm.	D257-54T	$> 10^{15}$	$> 10^{15}$	$> 10^{15}$
Surface Resistivity, ohms	D257-54T	5×10^{13}	5×10^{13}	5×10^{13}

We do believe, however, that these present electrical properties allow the polymer to be utilized for both power and communication wire. In fact, there are installations in service where Hi-fax is being utilized for tree wire, triplex wire, and power cable up to 5 kv. In all cases the abrasion resistance and cut-through resistance are the primary properties which were the basis for use of the material. Actual comparative figures for abrasion resistance are very difficult to determine because they are dependent on the method of test. We can report, however, that depending on the method of testing, Hi-fax will provide between four to one hundred times as much abrasion resistance as high methyl content polymers. Cut-through temperature on this polymer is in the vicinity of 105°C. This value is about 30°C. above that obtained for regular or high methyl content products.

Always of interest to any wire manufacturer is the stress crazing resistance properties of all polyethylenes. Because of this fact, a study (which is still continuing) was started in an effort to find the most satisfactory low methyl content polymer in this respect. The study of the effect of molecular weight showed much promise and the results of some of these tests are summarized in Table 5.

Table 5

RSV	Mw	F_{50}*
2.6	200,000	24 hours
4.1	330,000	648 hours
5.1	560,000	> 3000 hours

*Time for 50% failures in Igepal using the Bell Telephone Laboratory test.

We have recently encountered another type of stress cracking which occurs when a specimen is highly stressed in hot water (that is, 90°C.). Here, we do not have as conclusive a picture as exists with Igepal although we do know that the high Mw products are markedly superior.

Hi-fax is somewhat better in chemical resistance than high pressure polyethylenes. Of interest to the electrical industry, were tests where Hi-fax was exposed to an electrical-type oil (Suniso No. 6) at elevated temperatures and compared with stress resistant, high methyl content polymers. The results are given in Table 6.

Table 6

	Weight Gain One Week at 90°C.	Appearance
Hi-fax Type 1800	10%	No change
High-Methyl Polymer	Approx. 100%	Badly swollen, broken

This property suggests applications for Hi-fax where oil resistance is important.

Fabrication techniques for these high molecular weight, low methyl content polymers are, as would be expected, in the formative stages. To date, however, we have not encountered any serious problems and from our work we have been able to draw the following conclusions. Utilizing essentially standard polyethylene equipment (with the die design, screw design, and extruder conditions listed in Table 7) No. 22 wire has been coated at rates of 2,000 ft./min. with a 10-mil wall.

Table 7

Die	-	3/4 in. land with 3° taper
	-	Opening 7 mils larger diameter than wire O.D.
Screw	-	16 to 1 length
		4 to 1 compression ratio
		Decreasing depth constant pitch
		Exit water at 120°F.
Extruder	-	Davis Standard 2 inch
Die	-	550°F.
Barrel	-	550°F.
Throat	-	500°F.

Runs have also been carried out where the tubing technique has been used for jacketing 52 pair communication cable. No processing problems were encountered and the resulting Hi-fax cable had good handling characteristics (winding, etc.).

A large amount of work is left to be done in developing optimum fabrication techniques for wire coating. We know that quenching temperatures make a difference in the density of the final product (see Table 8).

Table 8

	Quenched Into Acetone and CO_2	Slow Cooled
Specific Gravity	0.945	0.963
Tensile Strength, lbs./sq.in.	2600	3800

The above are laboratory results and, therefore, are not completely comparable to commercial fabrication. They do, however, indicate that knowledge and control of the thermal history of the insulation or jacketing is important. Investigations along these lines are in progress in our laboratories to establish basic ground rules for such operations as extrusion and injection molding.

In summary, we can state that there is a long road ahead before all of the answers are in. We can state, also, with reasonable assurance that Hi-fax, with its electrical characteristics and its resistance to heat, abrasion, cut-through, and stress corrosion has properties which will be utilized in both the communication and power cable fields.

JBM
WOB:TDM
EWC

Table 9

PHYSICAL PROPERTIES OF INJECTION MOLDED HI-FAX

Properties	Units	ASTM Method	Hi-fax Types 1400	Hi-fax Types 1600
General				
Crystalline Melting Point	°C.		131	131
Molded Density	grams/cc	D792-50	0.947	0.945
Mold Shrinkage	inch/inch			
1/16 in. thick strip			0.025	0.026
1/4 inch. thick bar			0.038	0.045
Physical Properties				
Tensile Modulus	lbs./sq.in.	D638-52T		
23°C.		0.2 in./min.	92,000	105,000
60°C.			32,000	46,000
100°C.			16,000	22,000
Tensile Yield Stress	lbs./sq.in.	D638-52T		
23°C.		0.2 in./min.	3,450	4,400
60°C.			2,200	2,800
100°C.			1,300	1,700
Elongation at Yield	%	D638-52T		
23°C.		0.2 in./min.	20	20
60°C.			40	40
100°C.			42	42
Ultimate Elongation 23°C.	%		100-700	100-700
Stiffness in Flexure	lbs./sq.in.	D747-50	110,000	115,000
Rockwell Hardness	R Scale	D785-51	39	35
Shore Hardness	D Scale	D676-49T	66	65
Impact Strength - Izod				
Notched 23°C.	ft.lbs./in.notch	D256-54T	1.5-4.0	1.7-4.9
Unnotched 23°C.	ft.lbs./in.		>32	>32
Notched -40°C.	ft.lbs./in.notch		0.85	1.43
Unnotched -40°C.	ft.lbs./in.		>32	>32
Thermal Properties				
Heat Distortion Temp.	°C.	D648-45T		
66 p.s.i.			68	62
264 p.s.i.			45	44
Deformation Under Load 122°F.	%	D621-51		
2000 p.s.i. - 6 hours			16	10
Brittleness Temperature	°C.	D746-55T	<-60	<-60
Coefficient of Linear Expansion	in./in./°F.(70° - 180°F.)	Dilatometric	6×10^{-5}	6×10^{-5}
Specific Heat	calories/gram/°C. (40°C.)	Dilatometric	.50	.50
Thermal Conductivity	B.T.U./sq.ft./sec/°F./in.		.0008	.0008

Physical Properties (Continued)

Properties	Units	ASTM Method	Hi-fax Types 1400	Hi-fax Types 1600
Environmental Properties				
Water Absorption	%	D570-54T	0.03	0.03
Soluble Loss	%	D570-54T	none	none
Dimensional Stability		D756-46T		
Shrinkage - No Load 140				
140°F. - 100% R.H.	% Maximum		+0.60	+0.92
175°F. - 100% R.H.	% Maximum		-0.76	-0.40
Shrinkage - No Load				
212°F. Water ½ hour				
1/16 in.thick strip	in./in.		0.012	0.008
1/4 in. thick bar	in./in.		0.006	0.005
1/2 in. thick bar	in./in.		0.001	0.001
250°F. air - ½ hour				
1/16 in.thick strip	in./in.		0.034	0.022
1/4 in.thick bar	in./in.		0.022	0.020
1/2 in.thick bar	in./in.		0.010	0.013