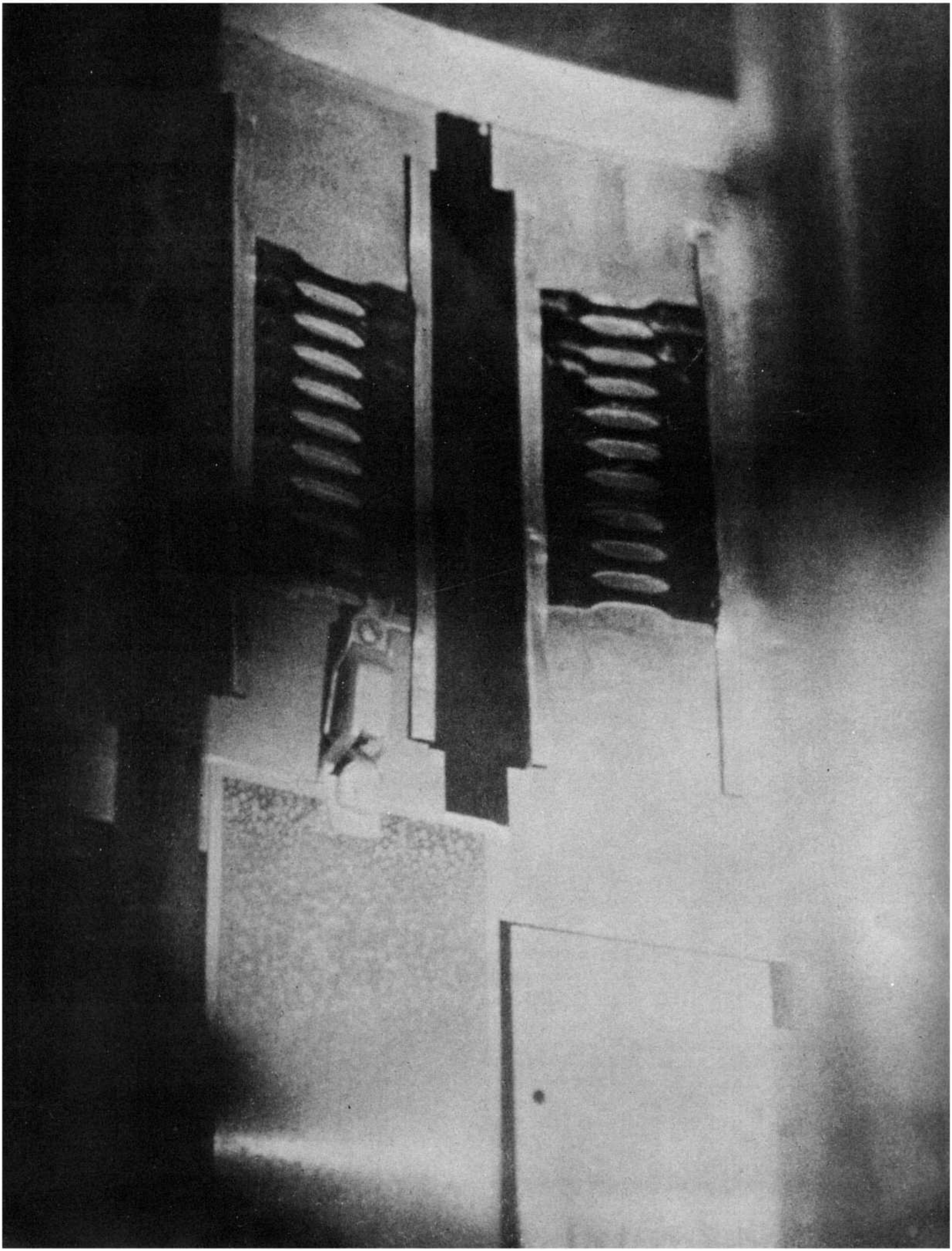


Cracks, which are but one sign of aging in the polyethylene sheath protecting cables, can cause havoc with the telephone system. To find out more about the complex reactions that lead to aging in plastics, scientists are turning to modern analytical tools.

Aging Problems of Plastics

V. T. Wallder

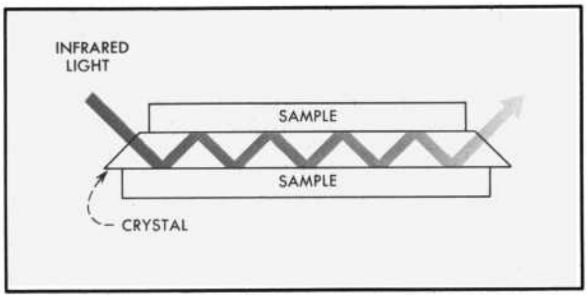
PLASTICS ARE AMONG the most widely used materials in the Bell System. Hundreds of millions of pounds of plastics are built into the telephone system each year and are expected to perform reliably for many decades. In practical applications the evaluation of their aging processes is still largely empirical, and a fuller understanding of the complex chemical and physical reactions that lead to aging is needed. To this end, new analytical approaches and testing methods are being developed at Bell Laboratories. A few examples have been selected to illustrate these methods.

In general, plastics tend to be unstable, reactive materials. Very few types exist in nature. They are mostly synthetic products, made by combining small molecules into large ones, known as polymers (from the Greek 'many parts'). Continued exposure to many of the common environments of our planet-sunlight, air, oxygen, water, cold, heat, and micro-organisms-can cause polymers to decompose into small molecules similar to those from which they were made. This process is called aging, and it leads to brittleness and eventual failure.

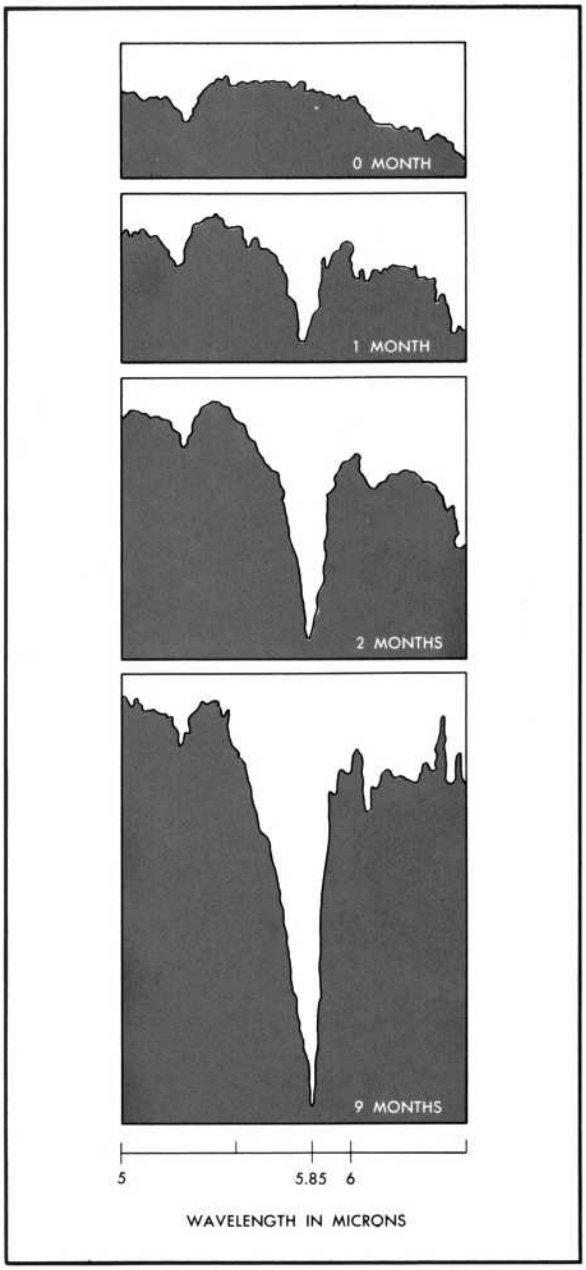
Reliability is a universally accepted design criterion for telephone equipment. The translation of this need into more precise engineering terms depends on the equipment and system. However, few applications allow the luxury of accepting much less than 20 years as an adequate life expectancy. Wire and cable intended for outdoor use must serve reliably for at least 20 years. An ocean telephone cable is expected to operate without attention at a reliability level that allows only two system failures in 20 years. Interior equipment such as that used in switching and transmission offices is designed for a life expectancy of 40 years.

Accelerated aging tests, which intensify the conditions responsible for degradation, have long been useful tools of the materials scientist. The first workable accelerated test procedures for polyethylene were announced by BTL 18 years ago. The report covered results of earlier outdoor and accelerated aging tests on a specific type of polyethylene compound. According to these tests 100 hours of accelerated aging was found to be equivalent to about one year of outdoor exposure. The results of these tests per-

Inside an accelerated aging device, plastic pieces and plastic-coated plates are exposed to ultraviolet radiation. A glass filter over the window of the oven-like structure removes those parts of the radiation spectrum that may harm an observer. The radiation is created by arcing carbon rods and simulates sunlight.



Two identical plastic samples under test are separated by a crystal that guides an infrared light beam and does not absorb its energy. Each time the light beam reflects from a plastic-crystal boundary, it penetrates slightly into the plastic and loses energy at those wavelengths where the material absorbs radiation. The plot of the emerging beam amplitudes at different frequencies yields the absorption spectrum of the plastic.



The detrimental effects of aging through outdoor exposure show up in the absorption spectrum of polyethylene. Increased absorption at 5.85 microns indicates the presence of carbonyl groups.

mitted the specification of a material with an expected minimum life of about 20 years. The first outdoor cables protected by this compound were put in service in 1947. To date there have been no failures due to weathering, and recent examinations show no signs of approaching failure.

The conclusions of the above-mentioned study were further extended recently, when samples of polyethylene cable sheath compounds exposed to outdoor conditions since 1941 were re-examined. Earlier figures were found to be overly conservative-it now appears that 100 hours of accelerated aging is equivalent to one to three years of outdoor weathering, making the anticipated lifetime of our currently produced cable sheaths more than 50 years.

Besides taking a long time (2000 hours and more), accelerated aging tests give only approximate results. Polyethylene fails in an outdoor environment because it absorbs ultraviolet radiation from the sun and undergoes oxidation. But the artificial light sources used in accelerated aging tests do not duplicate the spectrum of the sun, nor many of the other aspects of natural weather, and so the tests do not duplicate completely the sun's adverse effects. In addition, different plastic compounds absorb and are degraded by different parts of the sun's frequency spectrum, adding another factor of uncertainty to the analysis of the results of accelerated aging.

A new testing method now being studied at Bell Laboratories promises to overcome these difficulties. Since ultraviolet radiation first damages the exposed surface by inducing certain chemical changes, a test has been devised to detect these minute changes accurately. The quantitative results can then be related to the life expectancy of the material.

The breakdown mechanism in polyethylene originates in oxidation. Oxidation is detectable by the development of a carbon-oxygen chemical group known as carbonyl. The formation of this particular combination of carbon (from the plastic) and oxygen (from the air) is accelerated by the ultraviolet radiation present in sunlight. In the dark and at normal ambient temperatures, the reaction between polyethylene and oxygen proceeds slowly or not at all. Unexposed or unaged polyethylene contains little or no carbonyl. If the reaction with oxygen is permitted to continue for a long time, it eventually breaks up the originally long (high molecular weight) polymer chains into smaller and smaller pieces. Along with a decrease in its molecular weight, the toughness of the original material disappears; it becomes brittle and loses its usefulness.

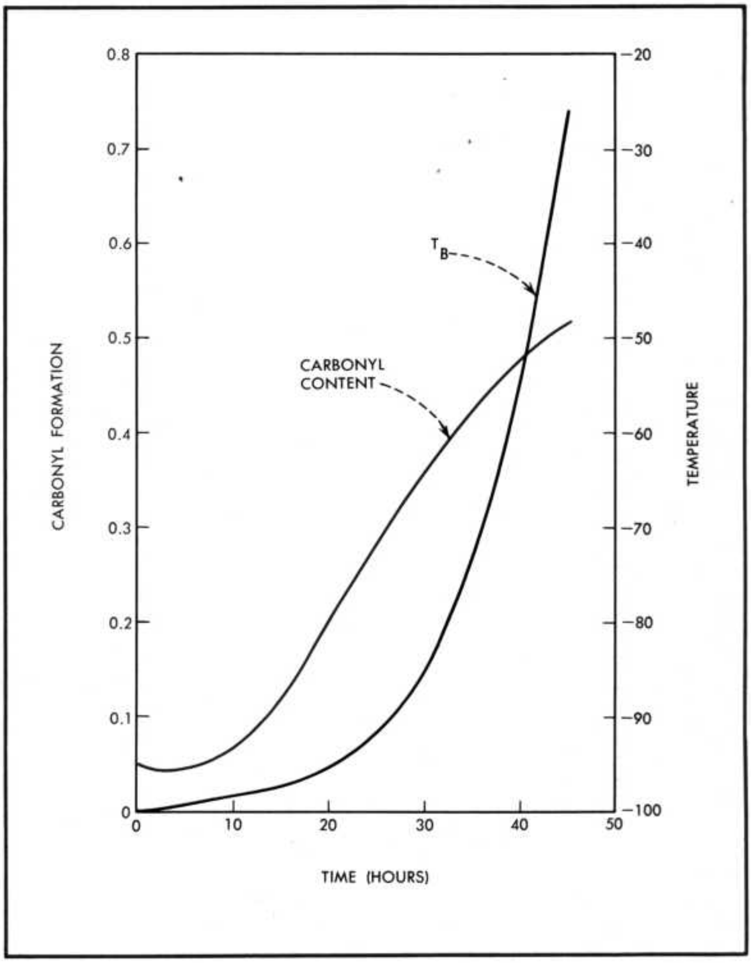
With the aid of multiple internal reflection spectroscopy in the infrared region, it has become possible to detect and to measure accurately the beginning of the oxidation process and its rate, and thus to predict the useful life of the material. The carbonyl group absorbs infrared radiation at 5.85 microns; therefore, any change in the spectrum of the material at this wavelength resulting from natural aging indicates the extent to which it has reacted with oxygen in the air. The aging period can be very short. Exposure to natural outdoor weather for about 40 hours will yield accurate data.

The test includes two measurements, one before aging and one after. Two samples of the material are used to sandwich a layer of crystal (see sketch on opposite page). The selected crystal does not absorb infrared radiation, and its main purpose is to guide the infrared beam. A ray of infrared light is directed into the crystal at an angle that forces the beam to reflect several times from the two crystal-plastic boundaries (thus the name, multiple internal reflection). Each time it reflects from one such boundary, the beam penetrates the plastic slightly and loses energy at those wavelengths where the material absorbs radiation. The attenuated beam that finally leaves the crystal is detected by infrared spectroscopy, and the amplitude of the beam at the frequencies of interest is plotted. The resulting curve represents the absorption spectrum of the plastic. An increase in its carbonyl content can be easily detected through changes at 5.85 microns.

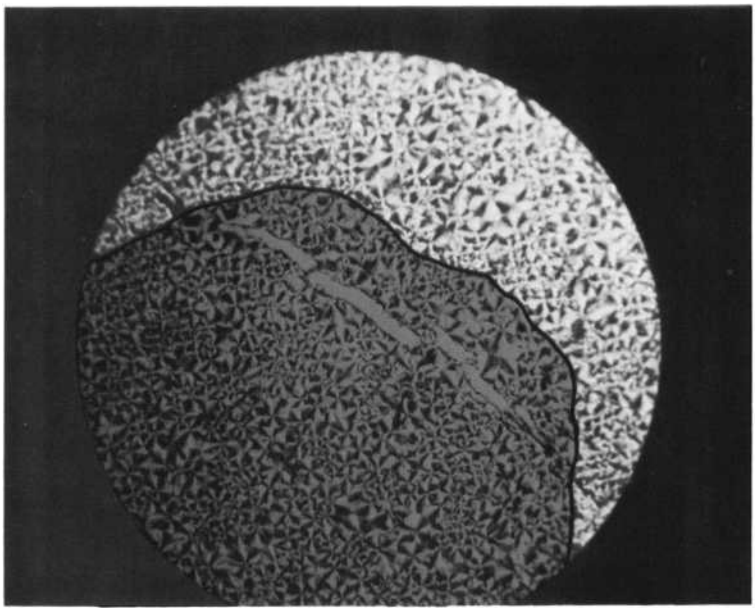
The light beam penetrates only a short distance into the plastic. This permits the testing of materials normally opaque to infrared radiation-for example, thick samples, and plastic containing carbon black.

The relationship between the carbonyl content of polyethylene and its brittleness at low temperatures has been firmly established (see curve on this page). Test results are even more conclusive for ABS (acrylonitrile-butadiene-styrene), a material from which station sets are molded.

In addition to outdoor weathering, plastics must be protected from thermal degradation. High temperatures may be encountered in some applications or during processing and can lead to premature failure of the material through oxidation. The usual preventive measure is the addition of anti-oxidant agents, whose efficacy can be measured with an oxygen absorption technique. In this test, the amount of oxygen absorbed by the plastic over a specified range of



Advancing surface oxidation of plastic makes it less suitable for low-temperature applications. The lowest usable temperature of polyethylene rose from -100 degrees Centigrade to -50 degrees Centigrade as its carbonyl content increased by a factor of four.



Environmental stress-cracking occurs in polyethylene in the presence of certain environmental conditions. This sample was treated with a detergent in the darker area shown. When the sample was stressed, cracks developed in the treated area.

The first three polyethylene strips, right to left, are stressed below their yield points, the fourth is at the yield point, and the elongated one is stressed much beyond its yield point. As H. M. Gilroy, Member of Technical Staff, applies an active agent to each of the strips, only the one stressed at its yield point breaks.

temperatures is measured, and the result can be used to predict the useful lifetime of the plastic. As better materials are developed, however, testing times become excessive.

A "differential thermal analysis" technique adopted recently by Bell Laboratories cuts down testing times from hundreds of hours to a few minutes. The procedure involves the measurement of the beginning of oxidation as the temperature is raised. Data resulting from differential thermal analysis agree almost perfectly with those obtained with the slower oxygen-absorption tests.

Besides the chemical reactions of oxidation and thermal degradation, physical reactions can cause failure in plastics.

A phenomenon of great interest to the Bell System is *environmental stress-cracking.* When some plastics are subjected to stress in the presence of certain environments, failure can occur. Without this environment, the material shows no sign of failure, no matter how long the stress is applied. On polyethylene, such common materials as soaps, wetting agents, detergents, and certain alcohols can cause rapid cracking and failure. In most plastics, the primary factor governing this phenomenon has been found to be molecular weight. Materials with low molecular weight stress-crack easily, while those with high molecular weight may not crack at all, or only after a much longer time. Intuitively, it is easy to understand that stress-cracking must also depend on the applied stress. But the exact nature of this dependence has only been established recently. It has been found that stressing in the region of the yield point of the material is critical. (The yield point is defined as a stress level beyond which the material will not regain completely its original shape when the stress is removed.) Experiments indicated that if the material is stressed below or much above its yield point in the presence of known stress-cracking agents, no failure will occur. It will crack only when the stress is near its yield point (see the photo on this page).

Knowledge of this factor then provides the engineer with an additional parameter when selecting the plastic. The normal use of the material should not induce stresses associated with its yield point, because they can lead to premature failure.

Designing for long life is a complex affair. The nature of the chemical and physical reactions that lead to early failure must be identified before any corrective action can be taken. The results of these tests amply justify the time and expense involved, because they contribute to the fuller scientific understanding of the behavior of materials from which our present and future telephone systems must be constructed.