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Stress-relaxation of cross-linked polyethylene at elevated temperature

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STRESS-RELAXATION
OF
CROSS-LINKED POLYETHYLENE
AT
ELEVATED TEMPERATURE
BY
RAIVO LUIK

A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE
AT
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1973

ABSTRACT

Polyethylene because of its excellent chemical, physical, mechanical and electrical properties, as well as its easy adaptability to extrusion, molding and other processes and its low cost has become a very widely used material for hundreds of applications. But, because it is a thermoplastic, it also deforms and flows when temperatures approach or exceed the crystalline melting point. This handicap, however, can be reduced by crosslinking the polymer chains and thereby converting the thermoplastic to a thermoset material. To further expand the possible uses of this popular material and to further improve the properties, fillers and antioxidants may be compounded in the polymer in the same manner as in rubber compounding.

In this investigation cross-linked polyethylene specimens were prepared containing different amounts of antioxidants and the resistance of these specimens to thermal and oxidative degradation at elevated temperature was tested by stress-relaxation techniques. It was observed that the presence of a very small amount of antioxidant does improve the performance of cross-linked polyethylene at elevated temperature.

APPROVAL OF THESIS
STRESS-RELAXATION
OF
CROSS-LINKED POLYETHYLENE
AT
ELEVATED TEMPERATURE
BY
RAIVO LUIK
FOR
DEPARTMENT OF CHEMISTRY
NEWARK COLLEGE OF ENGINEERING
BY
FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1973

PREFACE

The experimental work performed for this thesis was conducted at Bell Telephone Laboratories, Incorporated at Holmdel, New Jersey and at Murray Hill, New Jersey.

Newark College of Engineering supplied the specimen grips, the transducing cell, the recorder, and certain specific antioxidants. Use of a roll mill for compounding of test materials, the molding assembly, the hydraulic press, the test oven, the power supply, the specimen cutter, and the digital multimeter was granted by Bell Telephone Laboratories.

The author thanks Dr. W. J. Wenisch, his thesis adviser, for his invaluable assistance and patience.

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INTRODUCTION

Polyethylene was first produced by Imperial Chemical Industries, Ltd., during the 1930s in England as the result of experimentation with high-pressure chemistry of organic compounds. The first commercial plant was built by the British in 1939 and in 1941 ICI disclosed their process to an American delegation under the U. S. Government. Union Carbide and DuPont were contracted during World War II to build plants and start producing polyethylene in the United States with most of the production being used as insulation for high-frequency cables used in radar. After World War II the research efforts in polyethylene were accelerated and in early 1950s high-density polyethylene was discovered by Dr. Carl Zeigler in Germany, Standard Oil Company of Indiana, and Phillips Petroleum Company.

Polyethylene because of its excellent chemical, physical, mechanical and electrical properties has become a very widely used material for hundreds of applications. Some of the properties that have made it such a popular polymer are its excellent dielectric characteristics, lightness of weight, excellent chemical inertness to solvents, alkalies and acids, water resistance (low water transmission rate), flexibility and toughness over a wide range of temperatures, and freedom from odor, taste and toxicity. In addition to the above

properties polyethylene is relatively cheap in cost and the above properties can be adjusted or the resin can be tailored for other specific applications. It can also be processed at very competitive prices, it can be extruded with standard equipment or it can be molded in commercial injection-molding machines. As insulation and jacketing for wire and cable polyethylene has reduced the over-all diameter of these products. It is used as film for packing needs for many diverse products which remain flexible at high or low temperatures and will not embrittle or deteriorate with age.

But in spite of hundreds of excellent applications and its many desirable properties polyethylene has certain deficiencies that limit its still further utilization. The best known of these deficiencies are the poor resistance to deformation at elevated temperatures and the tendency to crack due to environmental and thermal stresses and poor resistance to hydrocarbon solvents at elevated temperatures. Because polyethylene is a thermoplastic, it deforms and flows when temperatures approach or exceed the crystalline melting point. This handicap, however, can be reduced by crosslinking the polymer chains and thereby converting the thermoplastic to a thermoset material. The resulting thermoset material has better thermal dimensional stability and stress-crack

resistance and also shows improvement in many other properties. The most successful methods for modifying polyethylene are irradiation and chemical crosslinking as a result of organic peroxide decomposition. The irradiation of polyethylene leads to greater insolubility, a change in tensile properties and better form stability at high temperatures, but this method is used for relatively thin sections and chemical crosslinking is more widely used since it is adaptable to thin or heavy cross-sections. The largest utilization of irradiated cross-linked polyethylene at the present time is in the form of heat shrinkable film used as poultry wrap and as overwrap for tight protective coverings. In addition to shrinkability, crosslinking of film by irradiation also gives the film a biaxial orientation, this gives the film its memory and also imparts it a crystal clarity, thereby making it particularly acceptable and popular for packing use.¹

Chemical crosslinking of polyethylene involves the formation of very highly reactive free radicals from the decomposition of certain organic peroxides. The free radicals form active sites on the polymer hydrocarbon chains so that additional carbon-to-carbon crosslinks can be formed.² So, for example, polyethylene mixed with dicumyl peroxide can be injection or compression molded with ordinary processing equipment at temperatures below

the activation temperature of dicumyl peroxide. Then the temperature of the processed specimen or part is raised past the activation point of dicumyl peroxide and polyethylene cross-links. The crosslinked polyethylene shows none of the earlier listed limitations of the thermoplastic polyethylene. Additional modification of the properties of the polymer may be made by adjusting the peroxide level or by use of different fillers. Some of the fillers that lead to tailor made properties are thermal, furnace, and channel blacks and inorganic fillers such as clay, alumina, silica, calcium carbonate and calcium silicate.² To further improve the properties of crosslinked polyethylene, especially to improve the thermal and oxidation degradation at elevated temperatures for prolonged times, antioxidants can be added. The effective utilization of combinations of antioxidants and organic peroxide crosslinking has placed polyethylene in the large market of wire and cable insulation. The estimated use of chemical crosslinked polyethylene has gone from less than 1 million pounds in 1959 to an estimated 75 to 100 million pounds in 1970. With ever-increasing demands for performance reliability and safety and with miniaturization and concentration of heat-producing components, degradation of polymers due to thermal aging is the most pressing problem. It is in wire and cable insulation applications that crosslinked

polyethylene has gained a major advantage due to its new higher continuous operating temperature range of approximately 90°C. It is also capable of handling 20 percent increases in current during emergency periods without shortening the life expectancy of the cable or wire. Another safety feature of chemical crosslinked polyethylene is the fact that it will not drip if subjected to an overload. With the ever increasing price of copper conductor another advantage of chemical cross-linked polyethylene is that it permits the use of smaller conductor for a given amperage of current.¹

The purpose of this thesis work was to further investigate the improvement in elevated temperature properties of chemical crosslinked polyethylene, that may or may not be achieved by using different levels of antioxidants while keeping the organic peroxide level constant. The prepared specimens were monitored by stress-relaxation measurements, a procedure used by H. L. Peritt.³ Stress-relaxation has been defined as follows:

Stress-relaxation is the time-dependent change in the stress which results from the application of a constant total strain to the specimen at constant temperature. The stress-relaxation at a given elapsed time is equal to the instantaneous stress resulting when the strain is applied, minus the stress at a given time. In other words, it is the decrease of stress due to internal relaxation under conditions of strain. Another term for this property is "stress decay."⁴

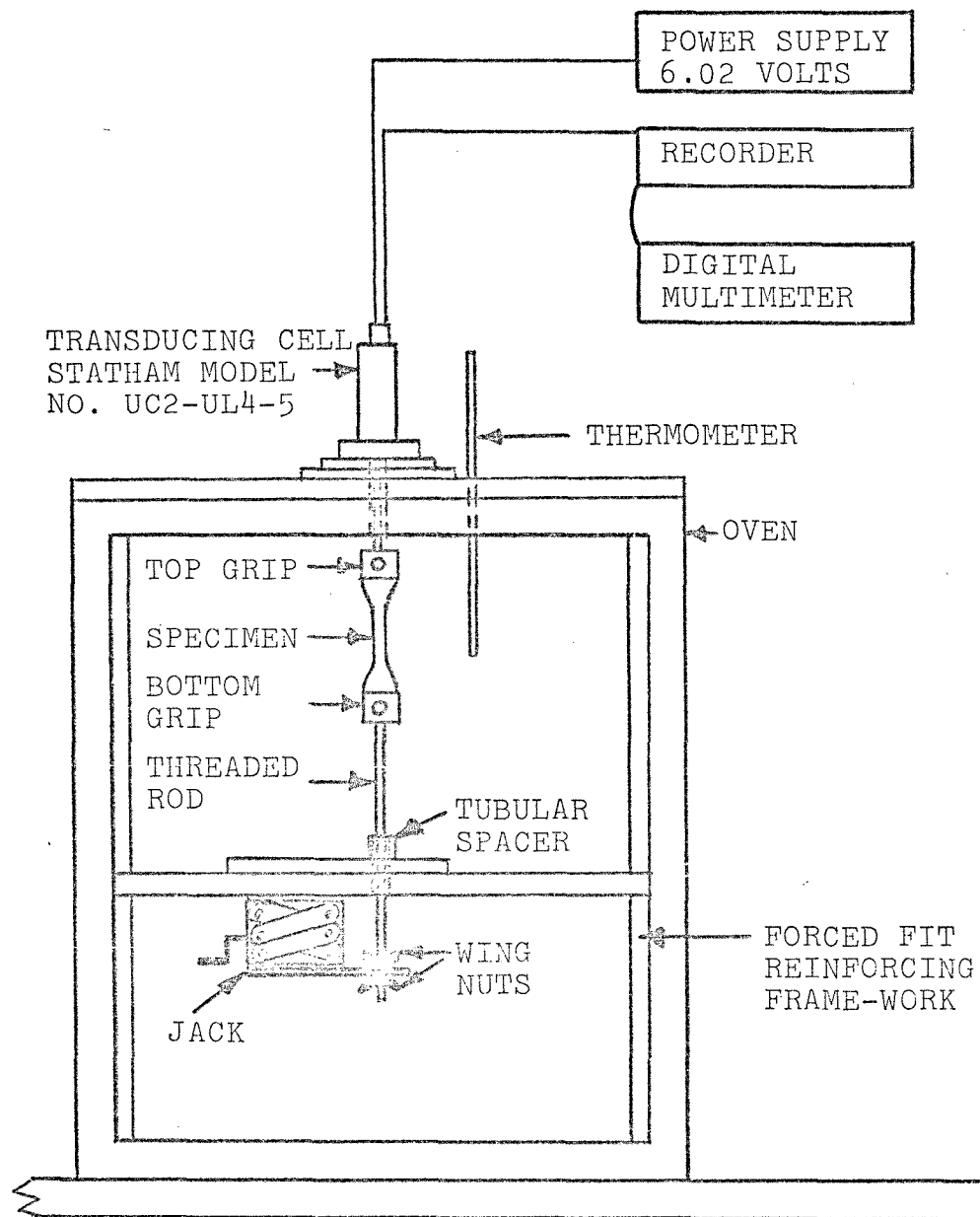
Although stress-relaxation measurements are more commonly used to study the degradation of rubber, it appears also to be a appropriate experimental technique for observing the stress-relaxation of cross-linked polyethylene. So, this technique was chosen to study the stress-relaxation of crosslinked polyethylene containing different amounts of antioxidants, as the specimens were elongated to a constant but arbitrary strain at elevated temperature.

CHAPTER I
APPARATUS AND TECHNIQUE
FOR
MEASURING STRESS-RELAXATION

1.1 Apparatus Design

The apparatus used to measure the stress-relaxation of the cross-linked polyethylene at elevated temperature is shown schematically in Figure 1. The apparatus was fabricated around an air circulating oven, STABIL-THERM Laboratory Oven manufactured by Blue M Electric Company, Blue Island, Illinois. The stainless steel oven had the following inside dimensions: height 18 inches, width 19 inches and depth 15 inches. The air circulating oven was thermostatically controllable to within $\pm 1^{\circ}\text{C}$. The top of the oven was reinforced with two 1.25 by 1.25 inch 1100 aluminum alloy angle bars spaced approximately 4.5 inches apart. On the aluminum angle bars was mounted a 4 by 4 inch 1100 aluminum alloy plate, 0.25 inch thick, with a hole in the center to accommodate the electrical transducing cell. The transducing cell, Statham Model No. UC2-UL4-5, Statham Instruments, Inc., 2230 Statham Boulevard, Oxnard, California, was bolted on top of the 4 by 4 inch plate. The plate was then bolted to the reinforcing bars on top of the

FIGURE 1
APPARATUS



oven so that the threaded hole in the bottom of the transducing cell was over the center of the hole in the oven top. The inside of the oven was also reinforced with a frame-work made of 1.25 by 1.25 inch 1100 aluminum alloy angle bars. The frame-work was so constructed that it was a forced fit against all inside surfaces of the oven. On the frame, 11.75 inches down from the top inside surface of the oven were bolted two angle bars running in the same direction as those on top of the oven. On these bars was bolted a 6.5 by 6.5 inch, 0.25 inch thick, 1100 aluminum alloy plate. In this plate were drilled holes for mounting the plate on the horizontal angle bars, holes for mounting a precision laboratory support jack to the bottom of the plate and a single 0.188 inch hole in straight line with the threaded hole in the transducing cell. On the bottom of the plate was bolted a micro precision laboratory support jack, Fisher Scientific Company Catalog No. 14-674-25, with a vertical travel range of 3.5 inches. The standard turning knob of the jack was replaced with a crank type of a handle, giving a larger mechanical advantage, so that the jack could be opened to its maximum in the minimum of time. The jack was so mounted that the handle pointed toward the left side of the oven. To the bottom side of the jack was bolted a 3 by 4.25 by 0.125 inch 1100 aluminum alloy plate. A 0.188 inch hole was drilled in the right hand

edge of this plate and the hole was lined up, by use of a steel rod, with the hole in the plate that the top of the jack was fastened to, the hole in the oven top and the threaded hole in the bottom of the transducing cell.

The transducing cell input wires were connected to a power supply, Programmable Regatron Model TR212A, Electronic Measurements Company of Eatontown, New Jersey. The power supply was calibrated to supply a input of 6.02 volts to the transducing cell and the power output was monitored with a digital multimeter throughout the experiment. The output wires of the transducing cell were connected to a Heathkit Servo Recorder Model EUW-20A, Heath Company, Benton Harbor, Michigan. The recorder was equipped with a motor capable of driving the chart paper (10 inch grid width) at a speed of two inches per hour. The cell output was also connected to a digital multimeter, Dana Model 3800A Digital Multimeter, Dana Laboratories, Inc., 2401 Campus Drive, Irvine, California, to provide a visual read-out of the transducing cell output and a second means of recording the stress-relaxation experiments. The digital multimeter readings were recorded on the chart paper as often as possible. During the first hour of the stress-relaxation measurement the digital multimeter was usually continuously monitored and the readings were recorded on the recorder chart.

1.2 Operation of Apparatus

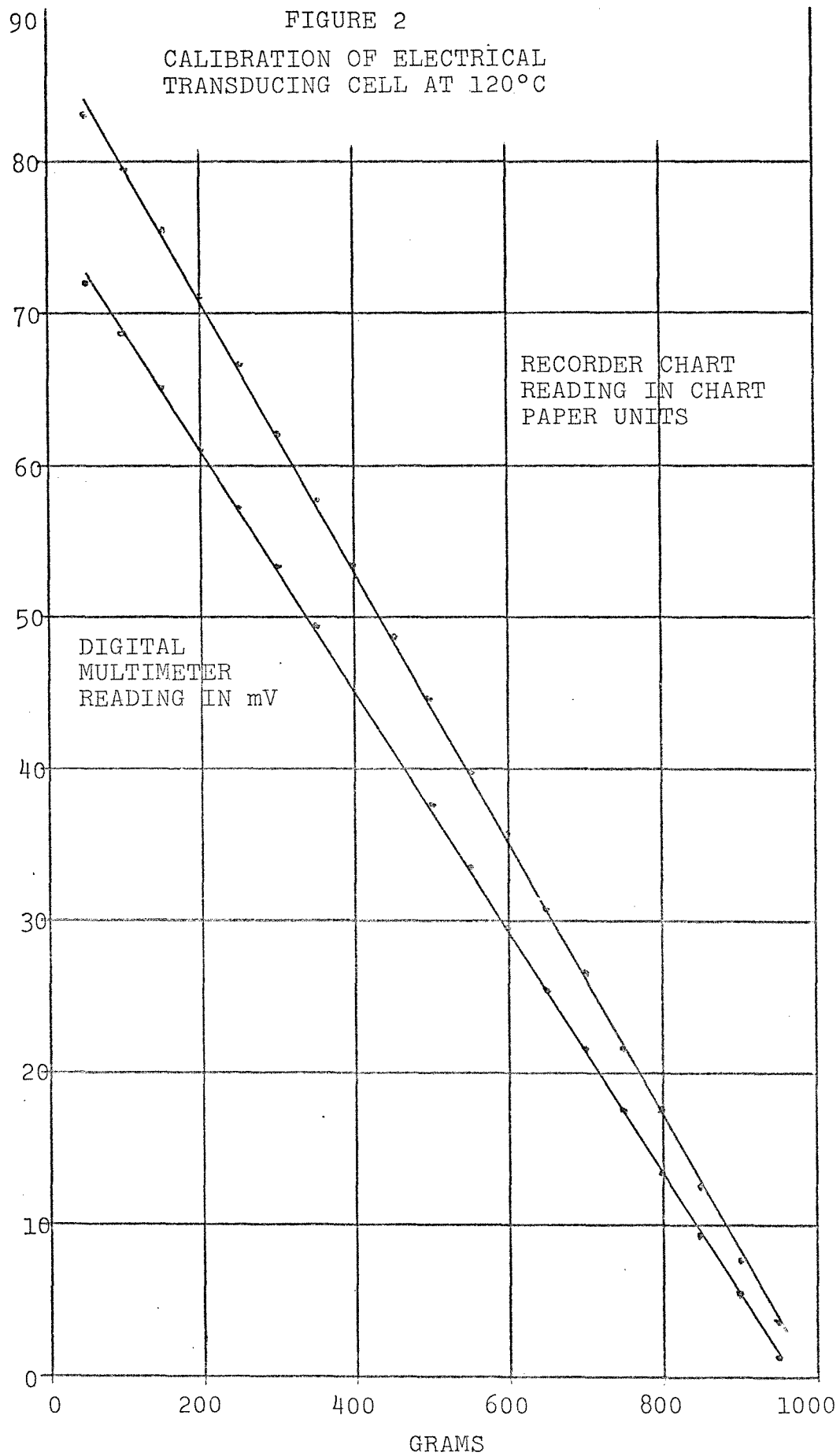
After assembling the apparatus shown schematically in Figure 1, the preliminary testing was started. The power supply was allowed to warm up and then calibrated again to supply an input of 6.02 volts to the transducing cell. This output to the cell was monitored throughout the experiments with the digital multimeter which was also used to monitor the output of the mercury reference cell of the recorder. The air circulating oven control was calibrated and the settings were recorded so that a desired temperature could be attained with a minimum of time. After all the equipment had been allowed to warm up, the transducing cell output with the oven at 120°C was found to be 79.7 millivolts. The temperature of 120°C was used throughout the experiments due to preliminary specimen testing discussed later in the thesis. With a digital multimeter reading of 79.7 millivolts for the output of the transducing cell, with no load, the base line of the recorder was so adjusted that this input to the recorder placed the recorder pen on the chart paper reading of 92. The chart paper was graduated from 0 on the right hand margin to 100 on the left hand margin on the 10 inch grid width paper. This means as a load is applied to the transducing cell the millivolt output will decrease and the recorder pen will travel from left to right. The chart paper reading of

92 and digital multimeter reading of 79.7 millivolts were used as reference points for all subsequent experiments. With the oven at 120°C, the top specimen grip, attached to a threaded rod was screwed into the threaded hole in the transducing cell bottom. The recorder reading and the digital multimeter reading were again recorded when the oven had stabilized at 120°C (this required approximately two minutes). The specimen grips used throughout these experiments were the same as used by H. L. Peritt,³ except that the grips were lined with uniform size pieces of 400 grade silicon carbide paper to prevent the test specimen from slipping. The calibration of the transducing cell was continued in the same manner by adding 50 gram weight increments to the top grip and recording the readings of the recorder and the digital multimeter. The results of the calibration procedure are shown in Table 1. A plot of these results in Figure 2, shows that the millivolt output is linear with the load applied to the transducing cell.

Next, preliminary testing was done to develop a standard procedure for handling actual test specimens, so that reproducible results could be obtained. After some trial and error the following procedure was adopted. First the apparatus is allowed to warm up and the air circulating oven is brought to 120°C. Using clean white

TABLE 1
CALIBRATION OF ELECTRICAL
TRANSDUCING CELL AT 120°C

WEIGHT ON TRANSDUCING CELL	RECORDER CHART READING IN CHART PAPER UNITS	DIGITAL MULTIMETER READING IN mV
TRANSDUCING CELL AT 120°C - NO LOAD	92.0	79.8
TRANSDUCING CELL PLUS TOP SPECIMEN GRIP	86.5	75.2
CELL + GRIP + 50g	83.0	72.0
100g	79.5	68.8
150g	75.4	65.1
200g	71.0	61.0
250g	66.8	57.1
300g	62.0	53.2
350g	57.9	49.3
400g	53.4	45.3
450g	48.8	41.2
500g	44.8	37.5
550g	39.9	33.5
600g	35.9	29.5
650g	30.9	25.5
700g	26.8	21.5
750g	21.8	17.5
800g	17.6	13.4
850g	12.6	9.3
900g	7.8	5.3
950g	3.8	1.3



cotton gloves the test specimen is placed between the silicon carbide paper lined test grips and the test grips are tightened. A measured tubular spacer, which is used as a gage block to control the amount of elongation of the test specimen, is placed over the threaded rod connected to the bottom grip. The door of the oven is then quickly opened and the threaded rod attached to the bottom grip, with the spacer held against the grip, is inserted through the hole in the top horizontal plate. Next a wing nut is threaded on the same rod with the wings up. Then the threaded rod attached to the top grip is screwed firmly into the hole in the bottom of the transducing cell, while the specimen and bottom grip are rotated in same direction so as not to twist the specimen. Next the threaded rod attached to the bottom grip is guided through the hole in the plate attached to the bottom side of the laboratory support jack. Then a second wing nut is threaded on the bottom rod with the wings down. At this time the bottom grip must be rotated so that it is in the same plane with the top grip and the specimen is free of twists. By adjusting the two wing nuts toward each other until tight, while keeping the bottom grip in the same plane with the top grip, the whole test fixture can be lined up with the transducing cell. Now by turning the modified handle of the jack, it is now possible to achieve various elongations of the

test specimen by using different size tubular spacers on the threaded rod immediately below the bottom test grip. To reduce the temperature drop in the oven while the specimen is being installed, one third of the right side of the oven opening was covered with a piece of Masonite bolted to the reinforcing frame. After a little practice, it was found that the specimen could be installed in the oven in approximately two minutes or less and with only a 8°C temperature drop. The specimens were always so installed that the jack was in a compressed position and so no stress was on the specimen. After closing the door, the oven reached 120°C again in less than 5 minutes. The specimen was allowed to stand at 120°C for 10 minutes which was timed with a interval timer. Then the oven door was opened and using cotton gloves, the specimen was elongated to the predetermined elongation by quickly rotating the jack handle to open the compressed jack until the tubular spacer on the threaded rod attached to the bottom grip stopped any further elongation of the specimen. During this elongation operation the oven temperature drop was approximately 2°C . The above procedure was used throughout the experiment.

CHAPTER II

SPECIMEN PREPARATION

2.1 Materials and Formulations

From the hundreds of different available types of polyethylene, crosslinking agent and antioxidant the following materials were found of interest and were chosen for the experiments:

Polyethylene

DYNK-1, Lot ET-4045, Union Carbide Corporation.

Crosslinking Agents

1. Dicumyl peroxide, "Di-Cup R", Hercules Incorporated.
2. Equal parts of DMDBH (2, 5 di-methyl 2, 5 di (tertbutyl peroxy)-hexane and sodium aluminum silicate, "Varox", Lot 4J4-6, R. T. Vanderbilt Company.

Antioxidants

1. Tetrakis [methylene 3-(3', 5'-di-t-butyl-4'-hydroxyphenyl) propionate] methane, "Irganox 1010", Batch No. 6549/0096/0, Geigy Chemical Corporation (now Ciba-Geigy Corporation).
2. 2, 2'-methylenebis (4-methyl-6-tert-butyl-phenol), "A. O. 2246", American Cyanamid Company.

3. Refined 4,4'-thiobis-(3-methyl-6-tert-butylphenol),
"Santonox R," Lot No. NK02-008, Monsanto Company,

The above materials were compounded into test specimen materials using the formulations shown in Table 2.

Graphical representations of the crosslinking agents and antioxidants used are shown in Figures 3, 4, 5, 6, and 7.

TABLE 2

SPECIMEN FORMULATIONS

GROUP 1

SPECIMEN	1	2	3	4	5	6
DYNK-1	100	100	100	100	100	100
DI-CUP	1.0	2.0	2.0	2.0	2.0	2.0
IRGANOX 1010	0	0	0.1	0.25	0.5	1.0

GROUP 2

SPECIMEN	7	8	9	10	11	12
DYNK-1	100	100	100	100	100	100
VAROX	6.0	4.0	4.0	4.0	4.0	4.0
IRGANOX 1010	0	0	0.1	0.25	0.5	1.0

GROUP 3

SPECIMEN	13	14	15	16	17
DYNK-1	100	100	100	100	100
VAROX	4.0	4.0	4.0	4.0	4.0
A.O.2246	0	0.1	0.25	0.5	1.0

GROUP 4

SPECIMEN	18	19	20	21	22
DYNK-1	100	100	100	100	100
VAROX	4.0	4.0	4.0	4.0	4.0
SANTONOX R	0	0.1	0.25	0.5	1.0

For the low density polyethylene, DYNK-1 was chosen because it is readily available and it is a good laboratory standard since it is supplied unpigmented and uninhibited. So, it is ideal for making standard specimens without introducing more variables into an already complicated experiment. "Di-Cup R" was chosen as one of the crosslinking agents because it was one of the first peroxides used to crosslink polyethylene and its chemistry is well known. When heat is applied to dicumyl peroxide it decomposes to produce two cumyloxy free radicals. These can react with polyethylene to produce cumyl alcohol while abstracting a hydrogen from the polyethylene and creating a free radical on the polyethylene chain. Two of these free radicals can combine to form cross-linked polyethylene. If dicumyl peroxide decomposes so as to form a methyl free radical and acetophenone, the methyl free radical will also abstract a hydrogen from the polyethylene chain and also create a free radical on the polyethylene chain. In both cases a carbon-to-carbon coupling will take place between the free radical sites on the polyethylene chains and produce a cross-linked polyethylene.⁵ "Varox" was chosen as a second crosslinking agent and it was used mostly as 4 parts minimum dosage of the 50 percent active powder, as recommended by the manufacturer.⁵

To protect a crosslinked polyethylene from deterioration upon aging under condition of elevated temperature an antioxidant must be added. It is important to remember that in a crosslinked polyethylene higher levels of antioxidant may be used than in thermoplastic polyethylene. But in choosing an antioxidant it must also be remembered that the antioxidant may react with organic peroxides and reduce the amount of crosslinking. Much research has been done on antioxidants, but there is still a lack of complete agreement on their exact mechanism of action. Good discussions on antioxidants may be found in Encyclopedia of Polymer Science and Technology, Volume 2,⁶ and in the 1971-1972 Modern Plastics Encyclopedia.⁷ In summary we can say that most polymers undergo oxidative degradation which may involve chain scission, crosslinking, or formation of oxygen-containing functional groups in the polymer or its degradation products. Antioxidants if properly used can avoid, minimize or slow these adverse oxidative effects. The oxidative processes usually involve the steps of initiation, propagation, chain transfer and termination. According to Shelton⁸ there are at least five different classes of oxidation inhibitors, with each class having a different mechanism for reducing the oxidation processes. These five different classes are peroxide

decomposers, metal deactivators, light absorbers, inhibitor regenerators, and chain stoppers or radical interceptors.⁸ For this series of experiments "Irganox 1010," "A.O. 2246" and "Santonox R" were used and they are listed in their respective groups in the 1971-1972 Modern Plastics Encyclopedia.⁷

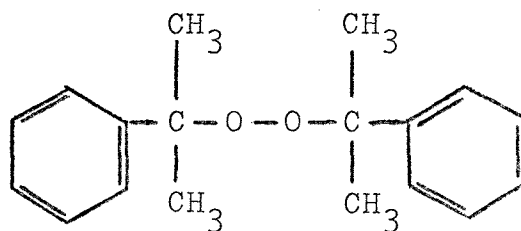
"Irganox 1010" is one of the newer antioxidants on the market and it is an interesting symmetrical molecule which includes four sterically hindered phenolic hydroxy groups. It has a very high molecular weight (1178) which gives it a low volatility and also a high melting point of 120°C making it easy to handle.⁹

"A.O. 2246" one of the older antioxidants, is a bisphenol and has a tendency to act as a radical interceptor.

"Santonox R" which is a purified dialkyl phenol sulfide was chosen because it is also one of the older antioxidants in use, it contains sulfur, and is supposed to be synergistic. Synergistic effect means that an antioxidant has been designed with structural features to take advantage of more than one type of action within a compound and the combined effect of such an antioxidant is greater than those of other types of antioxidants.

FIGURE 3

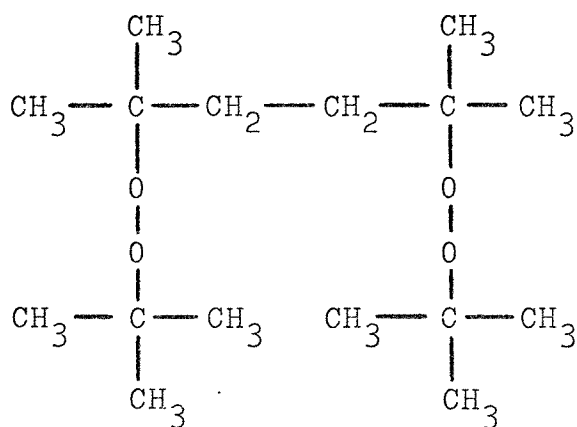
CROSSLINKING AGENT DI-CUP



Dicumyl Peroxide

FIGURE 4

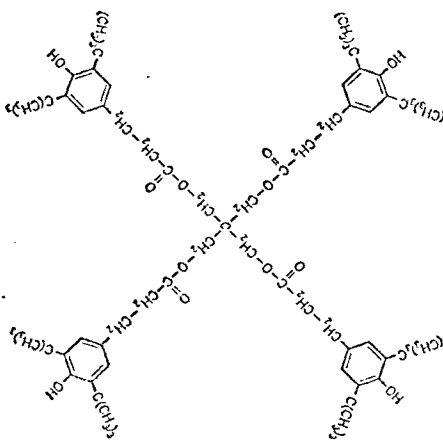
CROSSLINKING AGENT VAROX



2, 5-bis(tert-butylperoxy) - 2, 5 dimethylhexane

FIGURE 5

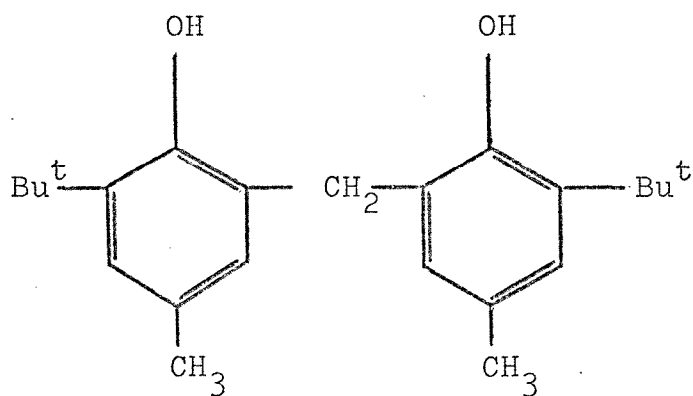
ANTIOXIDANT IRGANOX 1010



tetrakis[methylene 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)
propionate]methane

FIGURE 6

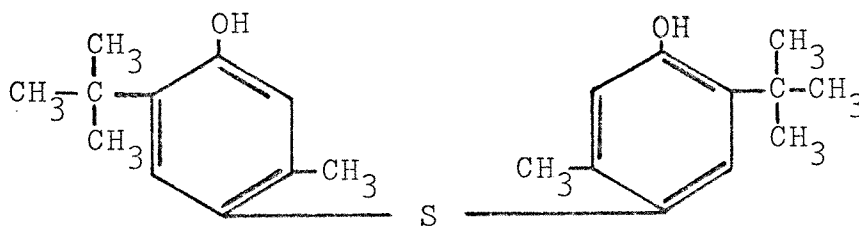
ANTIOXIDANT A.O.2246



2, 2'-methylenebis (4-methyl-6-tert-butylphenol)

FIGURE 7

ANTIOXIDANT SANTONOX R



4,4' - thiobis-(3-methyl-6-tert-butylphenol)

2.2 Milling Procedure

Test specimen material, one group at a time, was prepared in accordance with the formulations shown in Table 2, in the following manner. The 2-roll mill, manufactured by Farrel Birmingham Company Inc., Ansonia, Connecticut, was allowed to come to 121°C. The clearance between the rolls was adjusted to 0.015 inch and the weighed amount of polyethylene pellets, DYNK-1, was carefully poured on the rolls. When the polyethylene pellets showed signs of softening, the mill was activated and the polyethylene was masticated for 15 minutes. After the first few minutes of milling, the clearance between the rolls was increased to 0.025 inch, so that an active rolling blank is formed between the rolls after the material has formed a continuous band around one of the rolls. Any polyethylene pellets that had fallen on the clean sheet of paper below the rolls were incorporated into the batch on the mill at this time. During the milling the material was cut side to side at frequent intervals to homogenize the material. When a uniform melt was obtained, after 15 minutes of milling, weighed quantities of peroxide and antioxidant (when specified in the formulation of the particular specimen) were added. The mill was then run for an additional five minutes to allow for thorough mixing of the specified ingredients. After the five minutes, timed with an interval timer, the sheet of material

was stripped from the mill and placed on a clean sheet of paper to cool. After a few minutes of cooling, the sheet was cut into approximately 2 by 2 inch pieces to facilitate handling during the subsequent molding procedure. The small pieces of material were stored in clean, labeled, paper bags. After each specimen was milled, the mill was carefully cleaned and the paper below the rolls was replaced. All the specimens in a given group were prepared following the above procedure, during the same day.

During the milling it is important to remember that the mixing temperature of the mill must be above the fluxing temperature of the resin and yet below the temperature at which the peroxide decomposes rapidly. It is important to keep the temperature of the rolls at the lowest temperature at which the material will form a continuous band around one roll and not so high as to cause premature curing or scorch.

2.3 Molding Procedure

The milled material, all specimens in a group, were molded into sheets during the same day that they were milled, in the following manner. The mold used for all specimens was a smooth, clean, brass "frame" mold, outside dimensions 7.5 by 10 inches, inside 5.5 by 8 inches and 0.020 inch thick. The parting sheets were smooth, clean, lustrous aluminum alloy 1100 sheets 8 by 11 inches and 0.01 inch thick. The backing plates were smooth, hard aluminum alloy plates 9 by 10 by 0.375 inches. Both backing plates were equipped with a thermometer well. The press used was a Farrel Watson Stillman, manufactured by Watson Stillman Press Division, Farrel Birmingham Company Inc., Rochester, New York, and capable of exerting a pressure of at least 950 psi on the material to be molded.

The mold charge was calculated by multiplying the volume of the "frame" mold cavity by the approximate density of the material and adding a few grams of the milled material in order to completely fill the mold and produce a flash. After some preliminary molding it was found that a 15 gram charge produced the best test sheets.

After the parting sheets were cleaned with acetone and lint-free cloth, the following procedure was followed for molding all test sheets. One parting sheet was placed

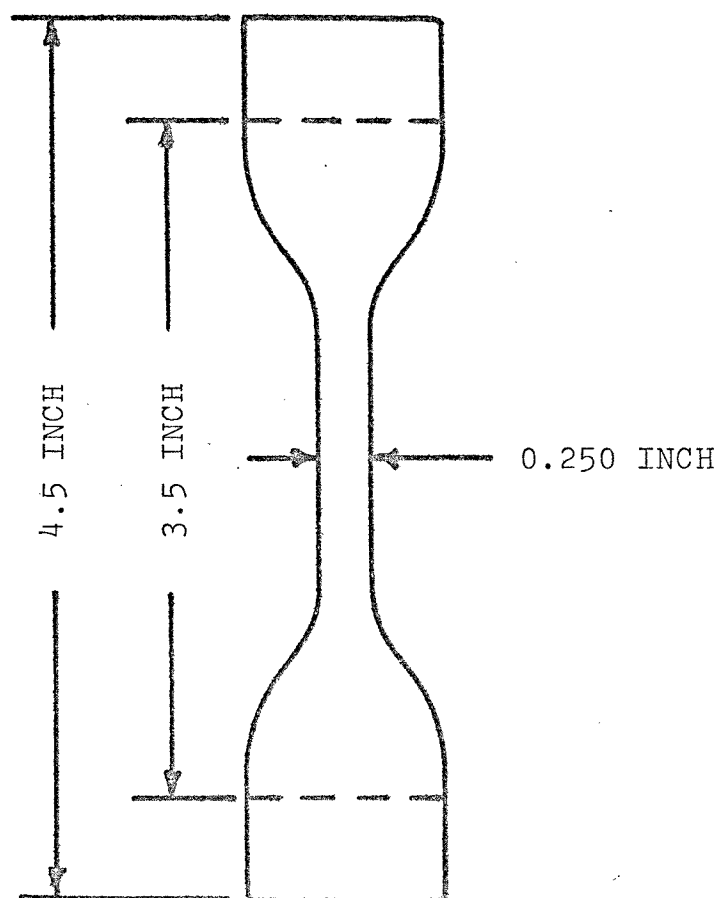
on one of the backing plates. On this sheet was placed the "frame" mold, on this the second parting sheet and on this the second backing plate. A thermometer was placed in a well in one of the backing plates, then the entire molding assembly was placed between the press platens whose temperature had been maintained at 177°C. While the molding assembly was being heated to 177°C, a 15 gram charge of the milled material was weighed. The heated molding assembly was then removed from the press and the 15 gram charge was placed between the parting sheets. The molding assembly was quickly returned to the press and pressure was applied (approximately 10 percent of the final molding pressure) so that both platens made light contact with the backing plates. When the temperature reached 177°C the total force was applied (950 psi). These conditions were maintained for 15 minutes, timed with an interval timer. The heat was then cut off, the flow of cooling water was started through the platens. When the molding assembly temperature decreased to 30°C, the pressure was released and the assembly was removed. The backing plates were removed, and the rest of the assembly unit was dropped into a cooling tank. The cooling tank was an overflow sink with running tap water at 16 to 25°C. After approximately 10 minutes immersion, the assembly unit was removed from the water, dried and the parting sheets were removed. The test sheet was removed

from the "frame" mold and the flash was trimmed. The molded sheet was then examined for obvious visible defects, labeled and stored in a clean paper envelope. If a sheet was defective a new one was molded from the same specimen formulation before proceeding to the next one.

2.4 Standard Test Specimen

From the sheets, molded in accordance with the procedure outlined in the previous paragraph, were cut standard dumbbell test specimens, see Figure 8. All test specimens were cut with ASTM D 412, Type C Die with a single stroke, so as to assure obtaining smoothly cut surfaces. The ASTM D 412, Type C Die was mounted in a Punch-Press-NAEF-Model B, made in Switzerland, distributed by MS Instrument Company, Inc., P. O. Box 185 Castleton on Hudson, New York. The cut specimens were marked while on a flat surface under no tension at the time, to provide a gage length of 3.5 inches, this gage length was used throughout the stress-relaxation measurements. Five thickness measurements were made and recorded for each specimen, three at the center and one at each end of the specimen. Specimens for which the differences between the maximum and minimum thickness exceeds 0.003 inch were discarded and new specimens were cut from the same sheet.

FIGURE 8
STANDARD TEST SPECIMEN



All test specimens were cut with ASTM D 412, Type C Die.

CHAPTER III

STRESS-RELAXATION TECHNIQUE

AND EXPERIMENTAL RESULTS

3.1 Stress-Relaxation Technique

As already mentioned in the introduction, stress-relaxation measurements are more often used to study the oxidative degradation of rubber at elevated temperatures than any other polymers. But, it also appears to be an appropriate experimental technique for observing the resistance to environmental degradation of cross-linked polyethylene at elevated temperature. Briefly, stress-relaxation is an experimental technique where a test specimen is elongated (or deformed) a constant amount at a predetermined temperature and the stress required to maintain this elongation is measured and recorded for a period of time. The maximum stress occurs as soon as the elongation takes place, and the stress decreases gradually with time from the initial maximum value. The stress decay with time is due to both physical and chemical processes. The physical relaxation or decay is due to chain entanglements between polymer molecules slipping past each other causing a relatively fast stress decrease on test specimens elongated to a fixed strain at elevated temperature. The chemical relaxation or decay is usually

many times slower and it involves the cleavage through oxidation of chemical bonds either along the main chain of the polymer or at crosslinks. So, simply stated, stress-relaxation occurs when a chain in a polymer which is carrying a load breaks. The rate of relaxation may be a function of the degradation rate of the polymer molecule or crosslink or both. The relaxation of stress is recorded and the results are plotted on semilog paper.

As stated earlier most of the theory used in this technique was developed by rubber chemists. A very detailed discussion of all the principles of mechanical behavior of polymers in terms of molecular architecture and dynamics is given by Arthur V. Tobolsky in Properties and Structure of Polymers. Most of the theory used in this experiment is discussed by Tobolsky in his chapter of mathematical treatment of linear viscoelasticity. Briefly, he states that if an ideal elastic body is elongated to a certain value of length L_o , and maintained at that elongation indefinitely, the equilibrium tensile force X required to maintain that length will be constant with time. The strain s_o is $(L_o - L_\mu)/L_\mu$, where L_μ is the original length; the stress f is X/A , where A is the cross-sectional area of the test specimen. The Young's modulus E is independent of the time at which X is measured and is given by $E = f/s_o$. The above relationships were

developed for an ideal elastic body, but for any real elastic body elongated to a certain value of length L_0 and maintained at that elongation indefinitely, the equilibrium tensile force required to maintain that elongated length will not be constant but will be a decreasing function of time $X(t)$. The strain for a real elastic body is again $(L_0 - L_\mu)/L_\mu$; the stress at any time t is $f(t) = X(t)/A$. From this was developed a new quantity, the relaxation modulus $E_r(t)$ which was defined by the following equation $E_r(t) = f(t)/s_0$. The above experiment developed and refined by Tobolsky¹⁰ is called relaxation of stress at constant extension and is the technique used in this work to observe the resistance of elongated cross-linked polyethylene specimens at elevated temperature.

The phenomenon of chemical stress relaxation itself was discovered in a study of cross-linked (vulcanized) rubber of the hydrocarbon type.¹¹ It was observed that at 100 to 150°C rubbers of the hydrocarbon type showed a rapid decay to zero stress at constant elongation. Until this observation it was believed that a cross-linked rubber network in the rubbery range of behavior should show little stress-relaxation, but should not decay to zero stress. After more study the phenomenon of decay to zero stress was attributed to a chemical rupture of

the rubber network due to the presence of molecular oxygen. During the discovery and study of chemical stress relaxation it was also observed that the relative stress-relaxation curves $f(t)/f(o)$, where $f(t)$ is the stress at time t , and $f(o)$ the initially measured stress, were found to be independent of the elongation at which the rubber was maintained. Through the above observations chemical stress-relaxation became a useful test procedure for measuring a chemical-bond cleavage in rubber networks. The rubber researchers concluded that the rate of chemical-bond cleavage is completely independent of forces acting on the rubber network or of the elongation of the network (up to at least 200 percent extension).

The above observations were utilized in this investigation to study the resistance of cross-linked polyethylene to thermal degradation. Polyethylene has one of the highest ratio of hydrogen immediately on the backbone to carbon and except for carbon to carbon bonds at chain ends and for those bonds which are adjacent to tertiary carbons at branchings, all other bonds in polyethylene have the same strength and the same chance of breaking under the influence of heat. So, the process of thermal degradation is primarily random. As is well known, the mechanism of thermal degradation of polyethylene involves the steps

of initiation, propagation, free-radical transfer and termination. Through our experiments we hope to see which combination of cross-linking agent and antioxidant yields the polyethylene with the best resistance to thermal degradation when observed by stress-relaxation experiments.

3.2 Experimental Results

The first few experiments performed were conducted to gain experience, to develop familiarity with the test apparatus, to develop a standard procedure for mounting and elongating the specimens so that reproducible results could be obtained. The early experiments were also used to establish a temperature level at which to test all the specimens in order to reduce the number of variables in the experiment.

The first specimen was placed in the test apparatus using the technique described in Chapter I at 150°C and it flowed immediately and could not be elongated. The temperature was then reduced in 10°C increments until at 120°C it was possible to mount a specimen in the apparatus, bring it to temperature equilibrium and then elongate the specimen and obtain an acceptable reading on the recorder. After some additional specimens were sacrificed at lower temperatures it was decided to use 120°C as the test temperature. This temperature was found to be the highest temperature that could be used to test every specimen that had been compounded and molded, while at the same time being high enough to give rapid results and also reduce the total duration of each test.

Once the test temperature had been determined and confidence had been established in the apparatus and procedure the real stress-relaxation testing was started. The test specimens had been prepared in four groups, their formulations are given in Table 2, a new group was prepared after all specimens in any one group had been tested. This was done so that the time that the specimens were stored in a laboratory at $72 \pm 5^\circ\text{F}$ was about the same for all groups. The relaxation of stress was recorded on the chart paper and during the first few hours, and when ever possible later, digital multimeter readouts were also recorded on the chart paper. After the specimen failed or the test was stopped the results were calculated and recorded in Tables 3, 4, 5 and 6 and then plotted on semilog paper. The ratio of stress at any time (t) divided by the initial stress (after physical relaxation) was plotted on the ordinate axis in logarithm scale and the time in hours was plotted on the abscissa in rectangular scale. According to the theory of first order oxidative scissioning of cross-link bonds a straight line should be obtained, the slope of which is related to the oxidation rate of the specimen. The experimental results for Group 1 specimens of Table 2 were calculated and recorded in Table 3 and then plotted in Figure 9. An examination of Figure 9 shows that

Specimen 4 (DYNK polyethylene specimen crosslinked with 2 parts Di-Cup and protected by 0.25 parts Irganox 1010) was the most resistant to thermal degradation followed by Specimen No. 5 (DYNK polyethylene specimen crosslinked with 2 parts Di-Cup and protected by 0.50 parts Irganox 1010).

The experimental results of Group 2 specimens of Table 2 were calculated and recorded in Table 4 and then plotted in Figure 10. An examination of Figure 10 shows that Specimen 10 (DYNK polyethylene specimen crosslinked with 4 parts Varox and protected by 0.25 parts Irganox 1010) and Specimen 9 (DYNK polyethylene specimen crosslinked with 4 parts Varox and protected by 0.10 parts Irganox 1010) were the most resistant to thermal degradation.

The experimental results of Group 3 specimens of Table 2 were calculated and recorded in Table 5 and then plotted in Figure 11. An examination of Figure 11 shows that Specimen 15 (DYNK polyethylene specimen crosslinked with 4 parts Varox and protected by 0.25 parts A.O. 2246)

and Specimen 13 (DYNK polyethylene specimen crosslinked with 4 parts Varox and unprotected) were the most resistant to thermal degradation.

The experimental results of Group 4 specimens of Table 2 were calculated and recorded in Table 6 and then plotted in Figure 12. An examination of Figure 12 shows that Specimen 19 (DYNK polyethylene specimen crosslinked with 4 parts Varox and protected by 0.1 parts Santonox R) was the most resistant to thermal degradation followed by Specimen 20. Examination of Figures 10, 11 and 12 shows that for Varox crosslinked DYNK polyethylene the best protection against thermal degradation is obtained if antioxidant in the range of 0.1 to 0.25 parts is used (see Table 2 for the formulations of Specimens 9, 10, 15, 19 and 20. Figure 9 shows that for Di-Cup crosslinked DYNK polyethylene the best protection against thermal degradation is obtained if antioxidant (Irganox 1010) in the range of 0.25 to 0.5 parts is used (see Table 2 for the formulations of Specimens 4 and 5.

Figure 13 shows the comparison of the plot of the best values from Figures 10, 11 and 12 and a blank (Specimen 8) and shows that Specimen 10 (DYNK polyethylene

specimen crosslinked with 4 parts Varox and protected by 0.25 parts Irganox 1010) was the most resistant to thermal degradation.

Figure 14 shows the comparison of the plot of the unprotected Di-Cup and Varox crosslinked specimens (Specimens 1, 2, 7, 8, 13 and 18) and the best Irganox 1010 protected specimens (Specimens 4 and 5). This figure shows what a remarkable improvement in resistance to thermal degradation 0.25 and 0.5 parts of Irganox 1010 can make when used with Di-Cup in DYNK polyethylene.

After reviewing all the plots of the tested specimens we can conclude that the best resistance to thermal and oxidative degradation at elevated temperature was shown by Specimen 4 (DYNK polyethylene specimen crosslinked with 2 parts Di-Cup and protected by 0.25 parts Irganox 1010) and Specimen 5 (DYNK polyethylene specimen crosslinked with 2 parts Di-Cup and protected by 0.5 parts Irganox 1010). For DYNK polyethylene specimens crosslinked with Varox the best resistance to stress-relaxation was shown by Specimen 10 (DYNK polyethylene specimen crosslinked with 4 parts Varox and protected by 0.25 parts Irganox 1010) and by Specimen 9 which also used 4 parts Varox but was protected by 0.10 parts Irganox 1010. In summary, we can say that the addition

of Irganox 1010 in the range of 0.1 to 0.5 parts does improve the resistance of cross-linked DYNK polyethylene specimens against thermal and oxidative degradation at elevated temperature when tested by stress-relaxation techniques. Irganox 1010 was found to be the best antioxidant tested and this is probably due to its very high molecular weight (1178) which gives it a low volatility.⁹

After spending so many interesting and rewarding hours with this experimental work some recommendations and suggestions were recorded for anyone interested in utilizing the same experimental technique. To get more interesting and useful results, after each sheet is molded a representative specimen should be cut and tested for antioxidant content. It is very easy to loose some of the antioxidant as the material is being milled. The second suggestion for improvement of test results would be to fabricate the test apparatus so that the specimen can be elongated in a fraction of a second from the outside of the oven without opening the door. An oven equipped with a glass window for observing the specimen would also be helpful.

TABLE 3

SPECIMEN FORMULATION AND RESULTS

SPECIMEN	1	2	3	4	5	6
DYNK-1	100	100	100	100	100	100
DI-CUP	1.0	2.0	2.0	2.0	2.0	2.0
IRGANOX 1010	0	0	0.1	0.25	0.5	1.0

S/S₀

SPECIMEN	1	2	3	4	5	6
TIME HOURS						
0	1.000	1.000	1.000	1.000	1.000	1.000
1	0.901	0.855	0.859	0.916	0.919	0.878
2	0.901	0.836	0.854	0.895	0.892	0.867
3	0.901	0.826	0.823	0.884	0.885	0.867
4	0.887	0.822	0.823	0.879	0.845	0.767
5	0.887	0.808	0.818	0.868	0.838	0.767
6	0.887	0.798	0.808	0.863	0.838	0.767
7	0.859	0.794	0.808	0.858	0.838	0.767
8	0.831	0.785	0.793	0.858	0.811	0.767
9	0.803	0.757	0.783	0.858	0.804	0.767
10	0.803	0.734	0.778	0.858	0.804	0.767
11	0.761	0.692	0.758	0.858	0.804	0.744
12	0.718	0.668	0.758	0.842	0.804	0.744
13	0.690	0.622	0.732	0.842	0.797	0.744
14	0.634	0.588	0.732	0.842	0.797	0.744
15	0.634	0.542	0.732	0.842	0.797	0.744
16	0.507	0.510	0.727	0.868	0.797	*
17	0.493	0.472	0.722	0.858	0.797	
18	0.479	0.426	0.717	0.858	0.797	
19	0.465	0.393	0.712	0.858	0.797	

* Recorder failure

TABLE 3 (CONT)

SPECIMEN TIME HOURS	S/S_0					
	1	2	3	4	5	6
20	0.451	0.355	0.707	0.847	0.797	
21	0.451	0.327	0.707	0.868	0.797	0.778
22	0.451	0.294	0.702	0.868	0.797	0.778
23	0.451	0.257	0.697		0.797	0.778
24	0.436	0.224	0.697		0.797	0.744
25	0.436	0.205	0.697		0.797	0.700
26	0.436	0.178	0.697		0.797	0.700
27	0.352	0.159	0.697		0.797	0.700
28		0.131	0.697		0.797	0.667
29		0.126	0.697		0.797	0.656
30		0.112	0.697		0.797	0.633
31		0.094	0.697		0.797	0.656
32		0.084	0.697		0.797	0.656
33		0.065	0.697		0.797	0.656
34		0.061	0.682		0.797	0.656
35		0.033	0.682		0.797	0.611
36		0.028	0.672		0.797	0.633
37		0.028	0.677		0.797	0.578
38		0.028	0.677		0.797	0.578

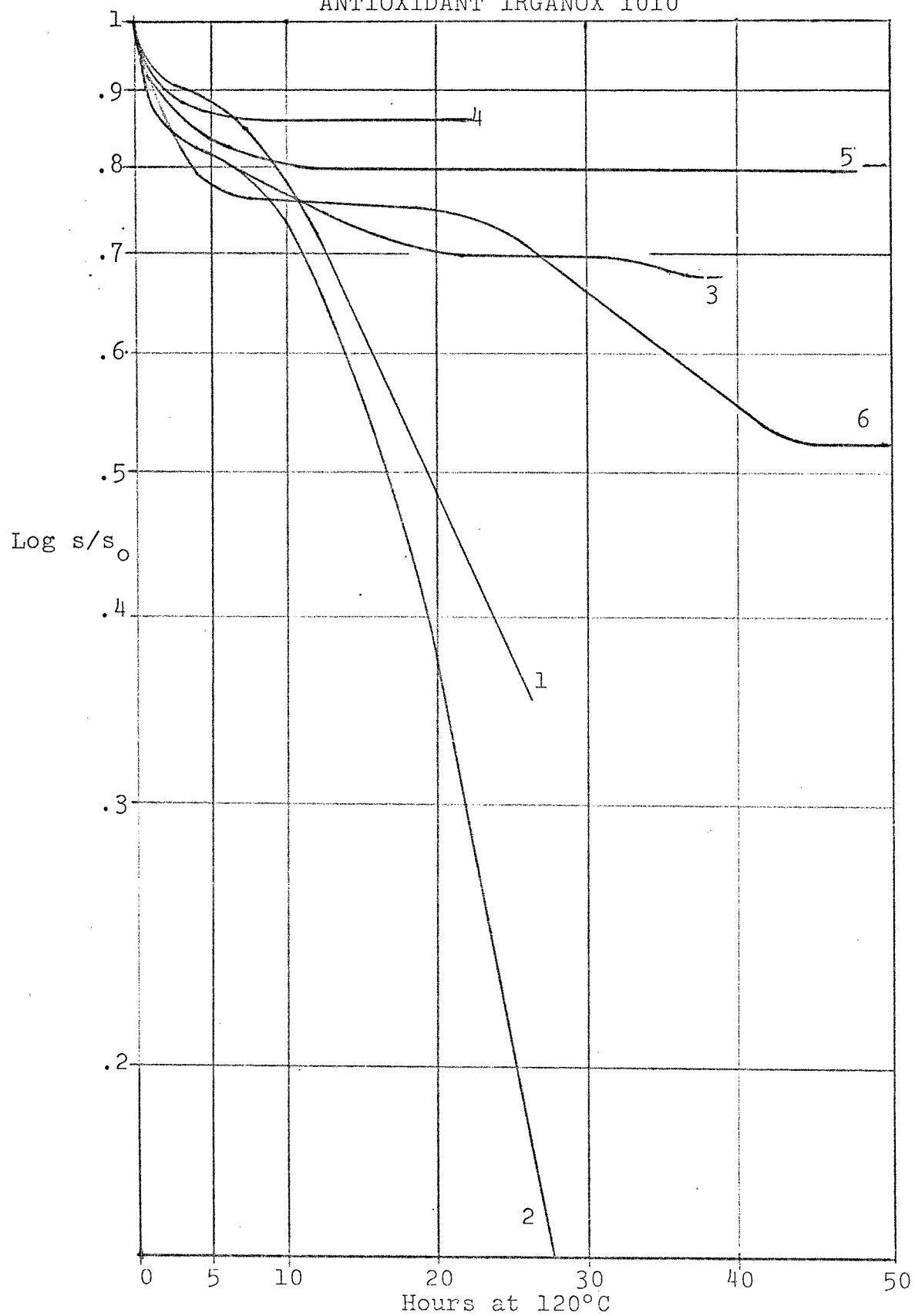
AGING OF DI-CUP CROSSLINKED DYNK
ANTIOXIDANT IRGANOX 1010

TABLE 4

SPECIMEN FORMULATION AND RESULTS

SPECIMEN	7	8	9	10	11	12
DYNK-1	100	100	100	100	100	100
VAROX	6.0	4.0	4.0	4.0	4.0	4.0
IRGANOX 1010	0	0	0.1	0.25	0.5	1.0

	S/S_0					
SPECIMEN	7	8	9	10	11	12
TIME HOURS						
0	1.000	1.000	1.000	1.000	1.000	1.000
1	0.780	0.692	0.809	0.719	0.533	0.375
2	0.700	0.569	0.797	0.695	0.533	0.313
3	0.620	0.446	0.786	0.707	0.533	0.313
4	0.540	0.400	0.774	0.659	0.533	0.313
5	0.440	0.323	0.714	0.659	0.533	0.313
6	0.320	0.292	0.714	0.659	0.533	0.313
7	0.260	0.277	0.714	0.659	0.466	0.313
8	0.100	0.169	0.714	0.659	0.500	0.125
9	0.020	0.108	0.690	0.659	0.500	0.125
10		0.092	0.678	0.646	0.500	0.125
11		0.077	0.655	0.634	0.500	0.125
12		0.077	0.655	0.622	0.500	0.125
13		0.077	0.655	0.622	0.533	0.125
14		0.077	0.643	0.622	0.533	0.063
15			0.643	0.622	0.533	
16			0.619	0.622	0.533	
17			0.607	0.622	0.533	

TABLE 4 (CONT)

SPECIMEN TIME HOURS	S/S_0					
	7	8	9	10	11	12
18			0.607	0.548	0.533	
19			0.559	0.561	0.366	
20				0.561	0.100	
21				0.597	0.100	
22				0.634		
23				0.646		
24				0.646		
25				0.646		
26				0.597		
27				0.573		
28				0.561		
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						

FIGURE 10

AGING OF VAROX CROSSLINKED DYNK
ANTIOXIDANT IRGANOX 1010

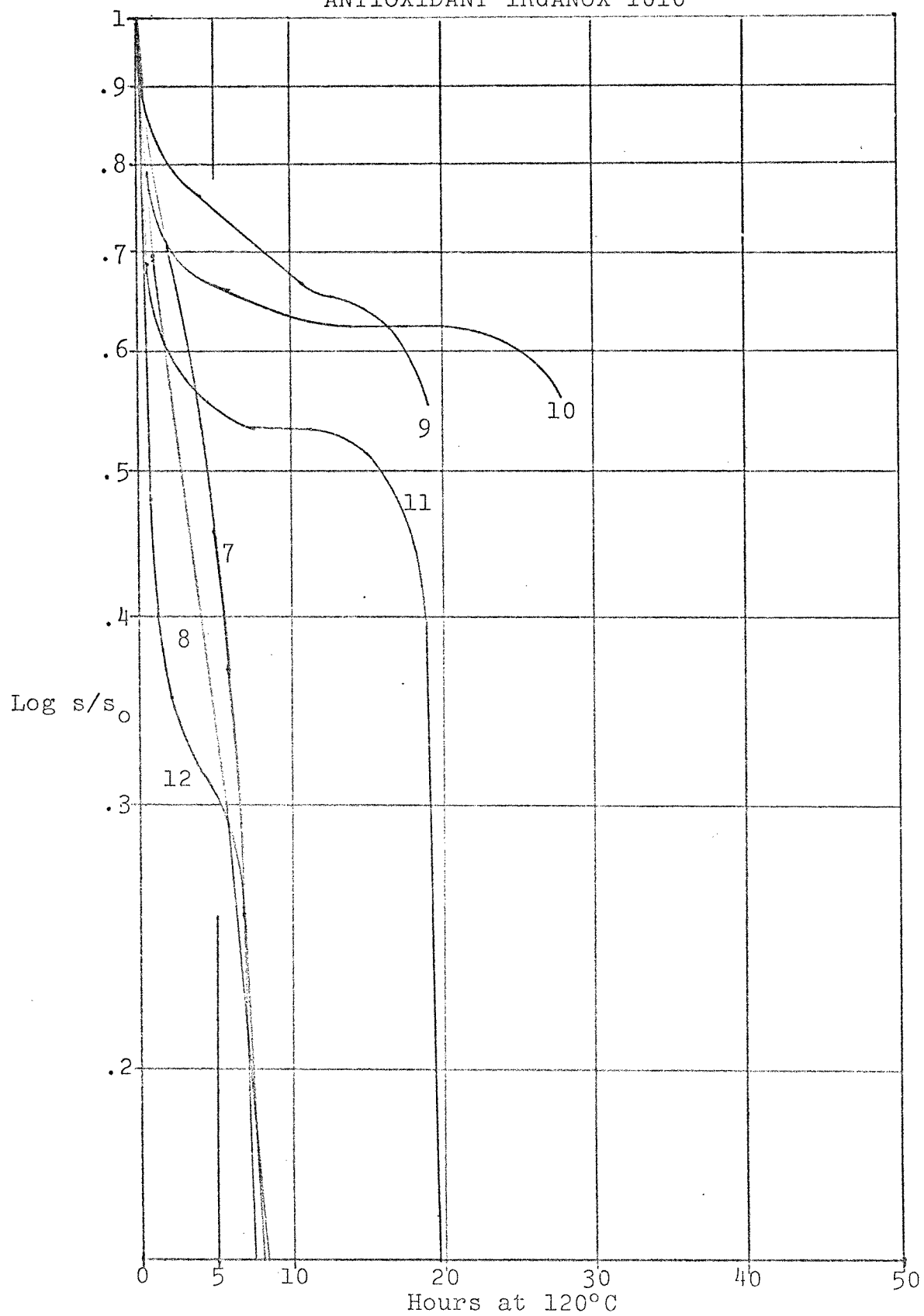


TABLE 5

SPECIMEN FORMULATION AND RESULTS

SPECIMEN	13	14	15	16	17
DYNK-1	100	100	100	100	100
VAROX	4.0	4.0	4.0	4.0	4.0
A.O.2246	0	0.1	0.25	0.5	1.0

	S/S_0				
SPECIMEN	13	14	15	16	17
TIME HOURS					
0	1.000	1.000	1.000	1.000	1.000
1	0.756	0.550	0.800	0.313	0.894
2	0.702	0.525	0.700	0.000	0.421
3	0.702	0.525	0.700		0.421
4	0.730	0.050	0.650		0.421
5	0.730	0.050	0.600		0.315
6	0.730	0.050	0.600		0.000
7	0.730	0.025	0.600		
8	0.675	0.025	0.600		
9	0.649	0.025	0.600		
10	0.649	0.025	0.600		
11	0.622	0.025	0.		
12	0.567	0.025	0.		
13	0.567	0.025	0.		
14	0.		0.		
15	0.351		0.600		
16	0.297		0.600		
17	0.216		0.500		
18	0.162		0.500		
19	0.081		0.500		

TABLE 5 (CONT)

SPECIMEN	S/S_0				
	13	14	15	16	17
TIME					
HOURS					
20			0.100		
21			0.100		
22			0.100		
23			0.100		
24			0.100		
25					
26					
27					
28					
29					
30					
31					
32					
33					
34					
35					
36					
37					
38					

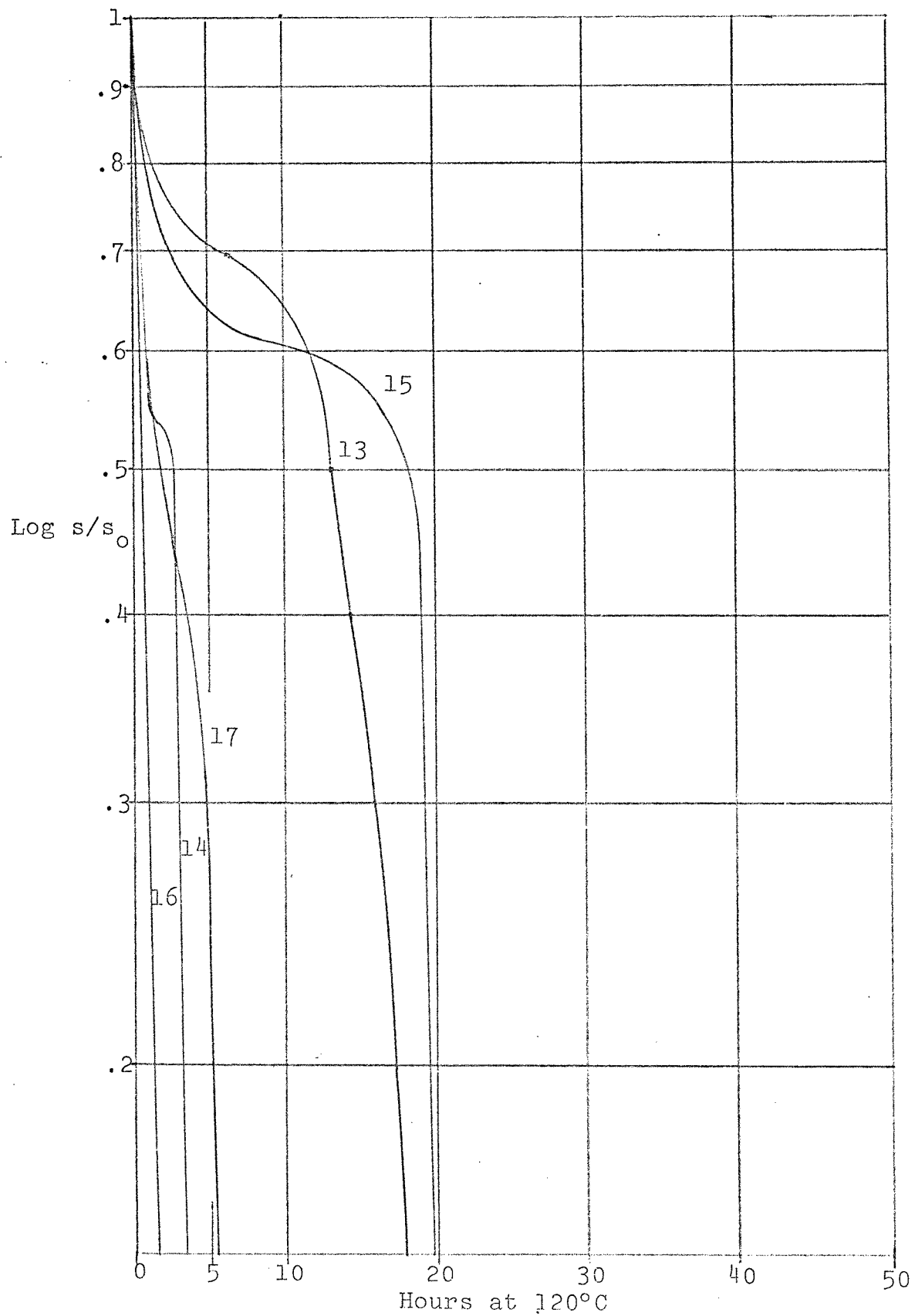
AGING OF VAROX CROSSLINKED DYNK
ANTIOXIDANT A.O. 2246

TABLE 6

SPECIMEN FORMULATION AND RESULTS

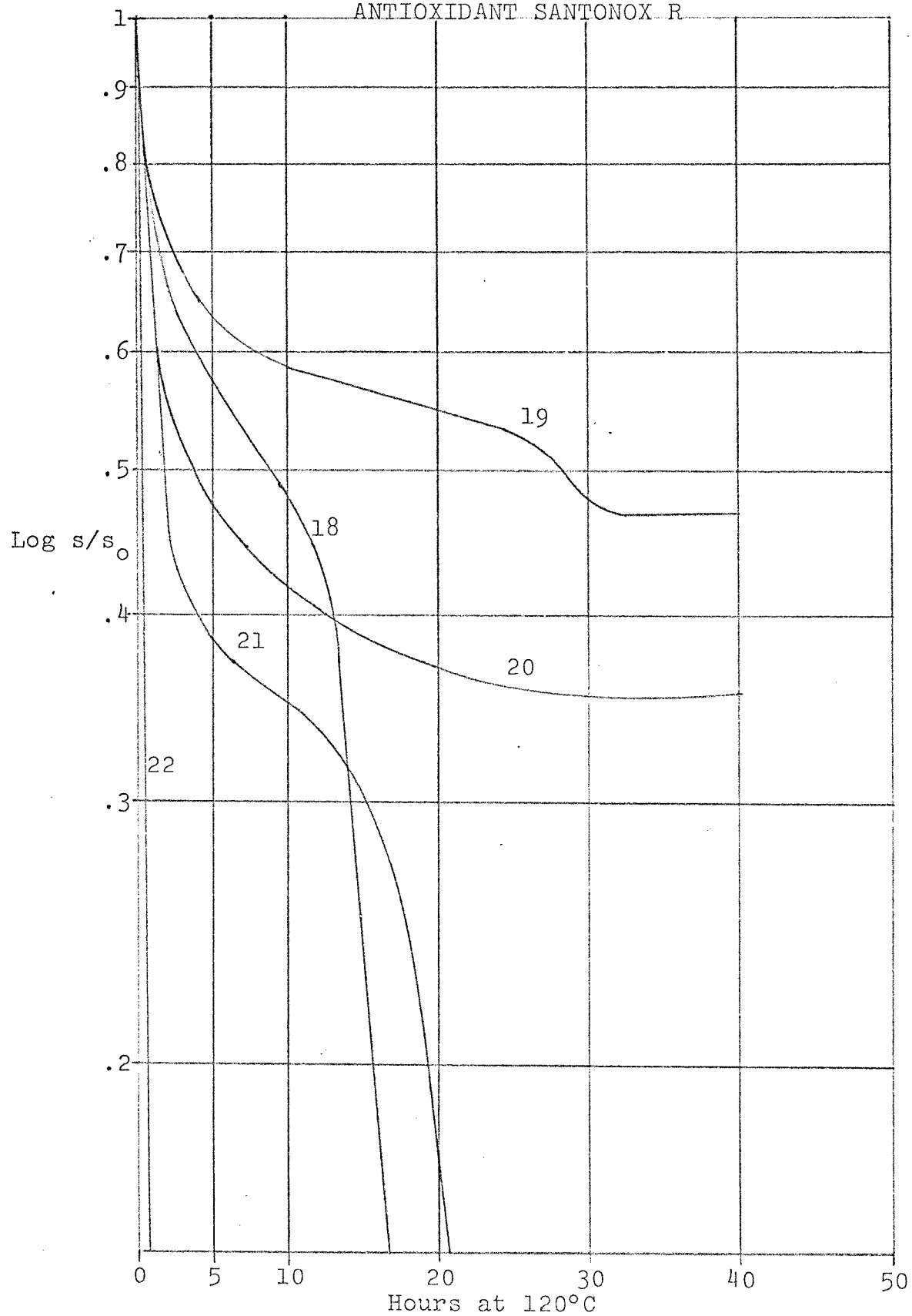
SPECIMEN	18	19	20	21	22
DYNK-1	100	100	100	100	100
VAROX	4.0	4.0	4.0	4.0	4.0
SANTONOX R	0	0.1	0.25	0.5	1.0

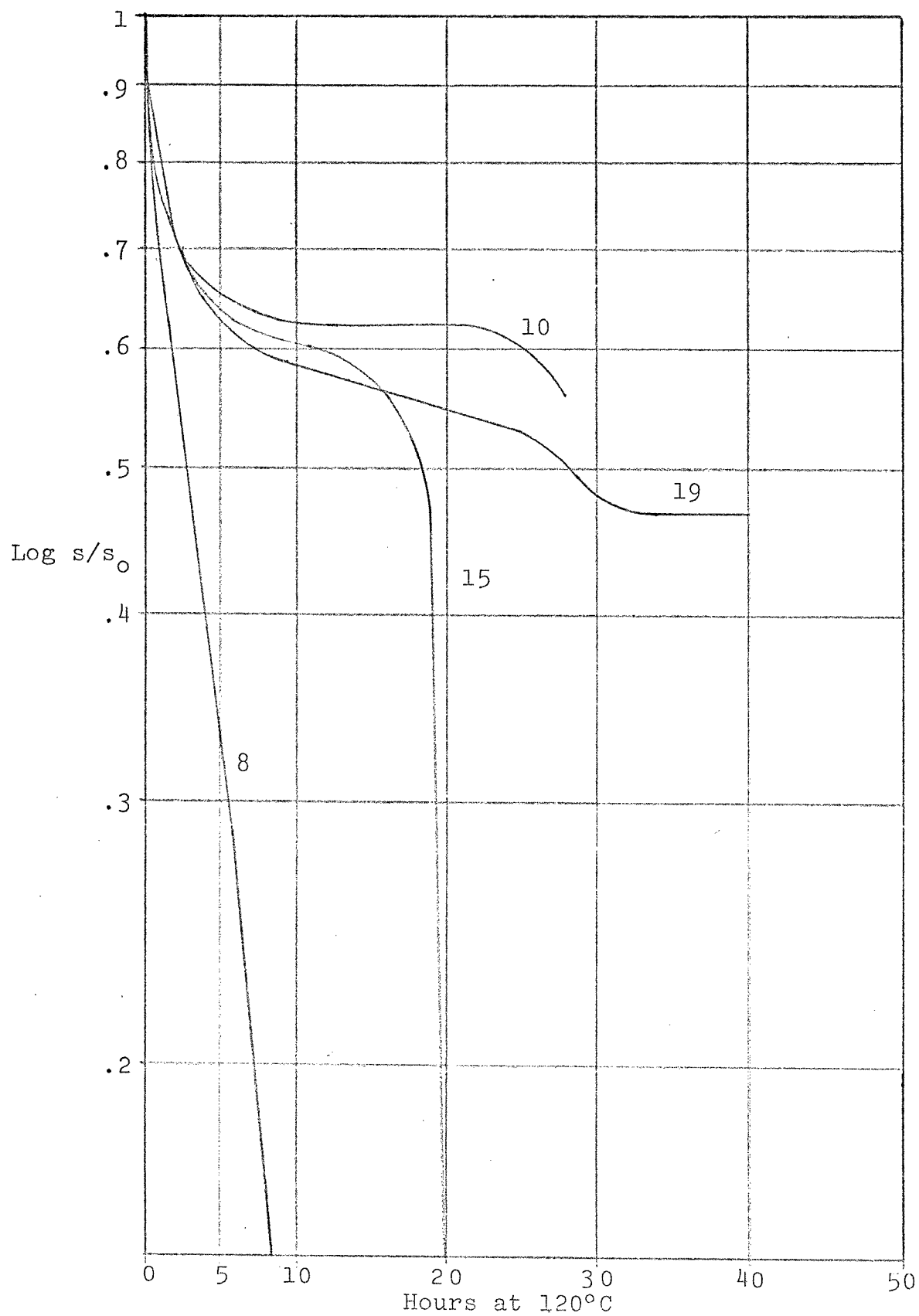
s/s_0					
SPECIMEN	18	19	20	21	22
TIME HOURS					
0	1.000	1.000	1.000	1.000	1.000
1	0.711	0.734	0.543	0.643	0.083
2	0.673	0.703	0.543	0.428	0.083
3	0.635	0.672	0.514	0.428	0.083
4	0.596	0.641	0.400	0.357	0.083
5	0.577	0.625	0.400	0.357	0.083
6	0.558	0.609	0.400	0.357	0.083
7	0.538	0.609	0.400	0.357	
8	0.519	0.594	0.371	0.357	
9	0.500	0.594	0.400	0.357	
10	0.481	0.594	0.400	0.357	
11	0.462	0.594	0.400	0.357	
12	0.404	0.578	0.400	0.357	
13	0.365	0.563	0.371	0.357	
14	0.269	0.563	0.400	0.357	
15	0.212	0.563	0.400	0.285	
16	0.192	0.563	0.400	0.285	
17	0.135	0.563	0.400	0.285	
18	0.096	0.563	0.400	0.214	
19	0.077	0.563	0.400	0.214	

TABLE 6 (CONT)

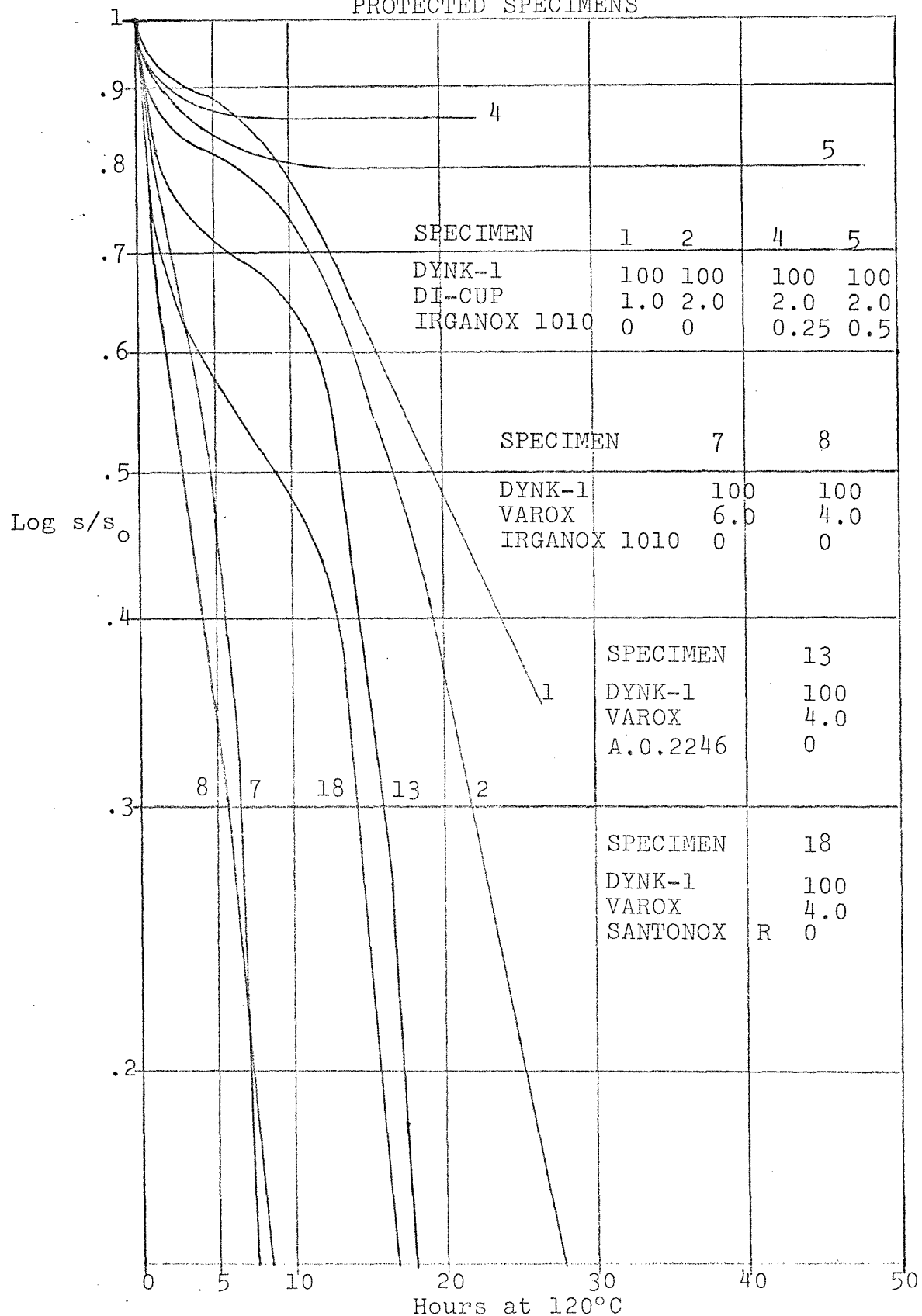
SPECIMEN	18	19	20	21	22
TIME HOURS					
20	0.077	0.547	0.371	0.214	
21	0.038	0.547	0.371	0.143	
22	0.038	0.547	0.371	0.071	
23	0.038	0.547	0.371	0.071	
24		0.547	0.371	0.071	
25		0.531	0.371		
26		0.516	0.343		
27		0.516	0.343		
28		0.516	0.371		
29		0.516	0.371		
30		0.469	0.343		
31		0.469	0.343		
32		0.469	0.343		
33		0.469	0.371		
34		0.469	0.371		
35		0.469	0.371		
36		0.469	0.371		
37		0.469	0.343		
38		0.469	0.343		
39		0.469	0.343		
40		0.469	0.343		

FIGURE 12

AGING OF VAROX CROSSLINKED DYNK
ANTIOXIDANT SANTONOX R

COMPARISON OF BEST VALUES FROM
FIGURES 10, 11 AND 12 AND A BLANK

COMPARISON OF UNPROTECTED DI-CUP AND VAROX
CROSSLINKED SPECIMENS AND BEST IRGANOX 1010
PROTECTED SPECIMENS



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