DEPARTMENT OF COMMERCE

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OF THE
BUREAU OF STANDARDS

S. W. STRATTON, Director

No. 38

THE TESTING OF RUBBER GOODS

[3d Edition]
Issued July 19, 1915

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THE TESTING OF RUBBER GOODS

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I. INTRODUCTION

The testing of rubber is a matter the importance of which is more generally appreciated now than formerly. The constantly increasing demand for rubber goods by the general public, by railroad companies, and other large consumers points to the necessity for developing standard specifications and tests for rubber as has been done in the case of iron, steel, cement, etc.

The purpose of this circular is to describe the methods of testing used at the Bureau of Standards, with the hope that sufficient interest may be aroused among manufacturers and purchasers of rubber goods to assist in bringing about that concerted action which is necessary for the standardization of tests, and to furnish the general public with information which will enable users of rubber goods to determine the quality of materials they secure.

1. SOURCES AND COLLECTION OF RUBBER

(*a*) SOURCES.—For the information of those who are unfamiliar with the subject a short account will be given of the processes through which rubber passes before reaching the factory.

In addition to the large quantity of rubber which is collected by natives from trees in the wild state, much is secured from plantations where rubber-bearing trees are cultivated according to scientific principles. This is generally known as "plantation rubber."

The principal rubber-producing trees, the countries where they are most abundant, and the commercial names of the rubber they produce are as follows:

Hevea: Para rubber. Brazil, Peru, Bolivia.

Micandra: Mixed with Para. Brazil.

Manihot: Manicoba or Ceara. Brazil.

Castilloa: Caucho. Central America, Mexico, Brazil.

Ficus: Assam, Rangoon, Java, Penang. Found principally in southeastern Asia.

Funtumia: Gold Coast Lumps, Ivory Coast Lumps, Congo, Cameroon. Eastern and central Africa.

Landolphia: Congo, Red and Black Kassai. Eastern and central Africa.

Hancornia: Mangabeira. Brazil.

Under the heading of industrial rubbers is included crude rubber available in commercial quantities, where the percentage of rubber is small compared with the impurities present. In such cases a process of purification is necessary before the rubber is ready for manufacturing purposes. Only two are of sufficient importance to warrant mention, viz:

Dyera Costulata: Jelutong or Pontianak. Occurs principally in Java.

Parthenium Argentatum: Guayule. Mexico.

The most important wild rubber, both in quality and quantity produced, is the Hevea, from which is obtained the Para rubber. It is found in Brazil, Peru, and Bolivia.

Taking into consideration all the wild rubbers, Brazil is the most important rubber-producing country. Of lesser importance may be mentioned Central America, Mexico, Central and East Africa, Malaya, and Java.

The most striking phase of the crude-rubber situation to-day is the tremendous growth of the plantation industry. The first experiments were started nearly 40 years ago, but it is only in the past 10 years that the cultivated rubber has become of commercial importance. In this short time the production of plantation rubber has grown from practically nothing until it is equal to that of the wild rubbers. Some idea of this growth may be gathered from the following table, which gives the production of plantation rubber in Ceylon alone:

TABLE 1

Ceylon Plantation Rubber

Year	Tons	Year	Tons
1903	19	1911	3200
1905	75	1912	5500
1907	250	1913	8000
1909	680	1914	14500
1910	1500		

Practically all of the plantation rubber comes from Hevea trees, only a small part of the total production being obtained from trees of other species, such as the Castilloa, Ficus, etc.

(*b*) COLLECTION.—Briefly stated, rubber is obtained in the following way: Incisions are made in the bark of the trees, and receptacles are placed under the incisions to collect the gradual flow of latex. The custom usually followed by natives is to coagulate or dry the latex by means of smoke or merely by exposure to the air. "Plantation latex" is coagulated by the addition of acid (generally acetic), after which the rubber is washed, sheeted, dried, and sometimes smoked. The smoking process has been adopted in an attempt to secure the valuable properties possessed by the wild rubbers, which are coagulated by smoking.

2. RUBBER SUBSTITUTES

No true rubber substitute—that is, no material possessing all the properties of rubber—has yet been produced. Synthetic rubber is identical in composition, etc., with the crude rubber, and so can not be called a substitute. It is not yet produced on a commercial scale. There are a number of so-called substitutes, however, that may be mixed with rubber to advantage in the production of certain articles.

The oil substitutes are of two kinds, namely, white substitute, produced by mixing corn, rapeseed, and cottonseed oils with sulphur chloride, and brown substitute, made by heating any of the above oils with sulphur.

The so-called mineral rubbers are either natural products, such as gilsonite, elaterite, etc., or the crude tar residue remaining after the distillation of petroleum. These substitutes are extensively used in the cheaper grades of insulated wire.

3. RECLAIMED RUBBER

On account of the large amount of waste vulcanized rubber or scrap available, and the high cost of crude rubber, the reclaiming of rubber has assumed such proportions as to constitute an industry in itself. By "reclaimed rubber" is not meant devulcanized rubber, although in some cases much of the free sulphur is removed. No process has yet been developed by which the process of vulcanization can be reversed and crude rubber reclaimed.

The old method of reclaiming consisted in grinding the scrap and removing the fibers and particles of metal, and other waste material, after which the rubber was mixed with oil, heated in ovens, and sheeted. In a more modern process the fibrous materials are destroyed by treatment with acid, after which the scrap is heated in ovens.

In a third method, known as the alkali process, which is carried out on an extensive scale, the old rubber is ground between rolls, particles of iron are removed by magnets, and the ground material is screened. The rubber is then heated in iron vessels containing an alkali solution, by which means free sulphur is removed and the fibrous matter destroyed, after which it is thoroughly washed to remove the alkali and dried by steam coils. It is then mixed between rolls, without the addition of oil, and sheeted.

It is said that rubber reclaimed by this process from carefully selected scrap is superior to some of the lower grades of crude rubber.

II. MECHANICAL RUBBER GOODS

The term "rubber," as commonly employed, does not refer to the commercially pure gum, but to a vulcanized compound as already described, which consists of gum, mineral matter or pigments, and sulphur, mixed in various proportions, according to the purpose for which it is intended. Mineral matter or the so-called fillers serve a very useful purpose both in cheapening the product and in adding certain desirable properties which could not otherwise be obtained. Their presence, therefore, should not be looked upon as an adulteration.

There is a limited demand for pure gum by the medical profession and a very considerable amount is used in the manufacture of stationery bands, elastic thread, etc., but the amount of rubber thus consumed is insignificant as compared with the enormous quantity used in the manufacture of mechanical rubber goods, such as automobile tires, hose, packing, and footwear. The methods of compounding rubber with various materials available constitute the technique of the manufacturing industry, and this phase of the subject is beyond the scope of this circular. It may be of interest to those unfamiliar with the subject to know that a properly vulcanized compound containing 40 per cent of high-grade rubber which is suitable for the best hose and packing may be stretched to about seven times its original length, and has a tensile strength of about 2000 pounds per square inch. On the other hand, there is an enormous demand for less expensive mixtures, such as are used for garden hose and the lower grades of packing.

The properties that are desirable in rubber depend in a great measure upon the use for which it is intended. For example, rubber intended for steam hose or steam packing should be of a composition to withstand high temperatures, while rubber for the tread of an automobile tire should offer great resistance to abrasion.

The real value of rubber in any case depends upon the length of time that it will retain those properties which are desirable, and it is a matter of common observation that rubber often deteriorates less rapidly when in use than when lying idle. Deterioration as indicated by loss of strength and elasticity is considered to be the result of oxidation, which action is accelerated by heat and very greatly by sunlight. Other things being equal, the better grades of rubber possess greater strength and elasticity, and may be stretched to a greater extent than the poorer grades, and they also deteriorate less rapidly. The physical properties of rubber, however, are subject to variation within wide limits, depending upon the proportion of gum present, the materials used as fillers, and the extent of vulcanization.

1. MANUFACTURE

Crude rubber as received at the factory is in the form of lumps of irregular shape and size, and contains varying amounts of impurities which have to be removed. These lumps are placed in a vat containing warm water, in order that they may become sufficiently soft to be handled by the washing rolls.

(*a*) Washing.—The washing rolls consist of two steel cylinders, about 12 to 18 inches in diameter, which revolve in opposite directions and at different speeds, their axes being parallel and in the same horizontal plane. These rolls are corrugated, and as the crude rubber is fed between them their action is such as to masticate the soft lumps and expose the impurities, which are washed out by a series of water jets and collected in a pan under the rolls. Two sets of rolls are used in this process. The first set breaks down the lumps while a large part of the impurities is washed out, and the second set, in which the rolls are closer together, completes the process of washing. After a sufficient number of passages through the rolls, the washed rubber has the form of a rough sheet of irregular shape, and contains considerable water, which must be removed before vulcanization.

This washing process is omitted in the case of plantation rubber which has already been washed before shipment.

(*b*) DRYING.—There are two methods in use for removing the water from washed rubber. The first is to hang the rubber sheets in a warm dry place—usually the attic—steam-heated pipes being used to maintain the proper temperature during cold weather. By this means evaporation takes place slowly, and considerable time is consumed in removing the moisture. This method is usually employed, as less skill is required than in the second and quicker method, in which vacuum dryers are used. It is claimed by some that a vacuum dryer softens and thereby injures the rubber, but a careful temperature control will avoid such injury.

(*c*) COMPOUNDING.—The rubber having been dried as described above, is "broken down" or worked through smooth steam-heated rolls, by which process it is rendered soft and plastic.

The rubber is now in condition to be compounded or mixed with sulphur and mineral matter and with reclaimed rubber or rubber substitutes if such are used. It is important that the sulphur and mineral matter be free, so far as possible, from grit and other particles of foreign matter, and for this reason such materials should be carefully screened.

The ingredients required for a batch having been weighed out in the definite proportions to produce a compound of the desired quality, the mixing is done with smooth rolls operated as in the washing process. Both steam and water connections are provided, so that the temperature of the rolls may be regulated to suit the condition of the rubber as it is being worked. The rubber gradually absorbs the sulphur and fillers which are added by an attendant. Such material as passes through without being incorporated with the rubber is collected in a pan and returned to the rolls. The temperature of the rolls is so regulated that as the operation of mixing proceeds the compound sticks to one of them in the form of a sheet. This sheet is cut with a knife, folded upon itself, and passed through the rolls again, the operation being repeated until the material shows a uniform color and is as nearly homogeneous as it is practicable to make it.

(*d*) SHEETING.—The next step in the process of manufacture depends upon the purpose for which the rubber is intended. If sheet rubber is being made, as for packing or for the tubes and covers of hose, the compound coming from the mixing rolls is passed through calender rolls. The calender consists of three steam-heated rolls, one above the other, which are so geared together that the middle roll revolves in the opposite direction from that of the other two. The rolls may be adjusted to form sheets of different thickness. The skeleton diagram in Fig. 1 shows the method of operation.

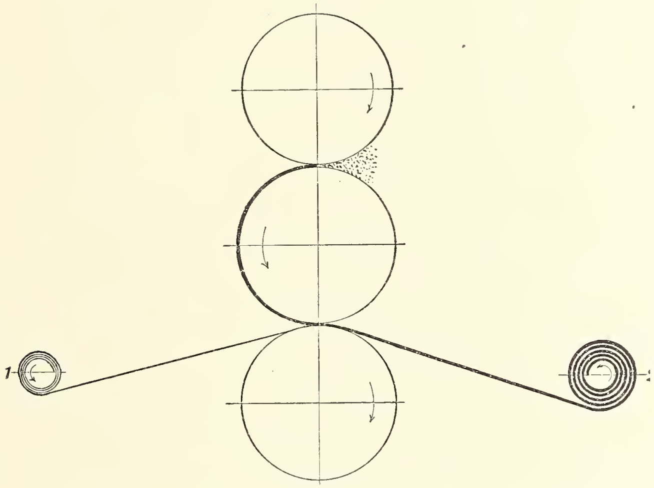


FIG. 1.—*Diagram showing operation of calender rolls*

Rubber is fed between the top and middle rolls, and by a proper regulation of temperatures the sheet adheres to the middle one while the top one remains clean. A strip of cloth is taken from reel 1 and passed between the middle and bottom rolls to reel 2.

The sheeted rubber as it passes between the middle and bottom rolls is received by the cloth and carried to reel 2, upon which they are wound together, the cloth preventing the layers of rubber from adhering. The sheet may be cut into strips of any desired width by knives which press against the middle roll.

Sometimes several calendered sheets are rolled together to form a single sheet. In the case of high-grade rubber hose, such as fire hose, the object is to avoid flaws in the finished sheet. The rubber is now ready to be vulcanized or worked into hose or other fabricated articles.

(*e*) "FRICTION."—What is known as "friction" in the case of rubber hose, rubber belting, and other articles which are made up with superimposed layers of canvas, is the soft rubber compound which is applied to the canvas, and by means of which the different layers or plies are held together.

The canvas is first dried by being passed over steam-heated rolls, after which the friction is applied by means of rolls which are operated in the manner just described and illustrated in Fig. 1.

The friction is fed between the top and middle rolls and forms a coating on the surface of the latter. The canvas to be frictioned is taken from a reel, passed between the middle and bottom rolls, and wound onto a second reel on the opposite side of the rolls.

In the case of the friction calender, the bottom roll revolves at about two-thirds the speed of the middle roll, thus causing a wiping action which forces the friction well into the meshes of the canvas.

(*f*) CUTTING THE CANVAS.—Canvas for use in making rubber hose is usually cut on the bias from strips 40 to 42 inches wide into pieces long enough so that when placed end to end and lapped the resulting strip is just wide enough to produce the necessary number of plies on the hose. There is no waste when cutting on the bias and the finished hose is more flexible than when the canvas is cut straight. On the other hand, when the canvas is cut straight, there is more or less waste on account of the last strip, which is often too narrow to be used. This method of cutting, however, produces the stronger hose, and a hose which will not expand as much, and which will elongate under pressure, avoiding the objectionable feature of longitudinal contraction which is noticed in hose made with bias-cut duck.

(*g*) VULCANIZING.—Crude rubber is greatly affected by changes in temperature, becoming stiff when cold and soft and sticky when warm.

Goodyear discovered, in 1839, that if crude rubber to which sulphur had been added was heated to a temperature above the melting point of sulphur, it combined with the sulphur, became very much less susceptible to temperature changes, and at the same time gained both in strength and elasticity. This important discovery may be said to mark the practical beginning of the rubber industry, although crude rubber had been previously used to a limited extent as a waterproofing material. The process whereby sulphur is incorporated with rubber is popularly known as "vulcanizing."

In 1843 Thomas Hancock patented a process in which rubber was vulcanized by dipping it in a bath of molten sulphur. In 1846 Parkes patented his process for vulcanizing with sulphur chloride, a process of great industrial importance, since it requires no heating. These three processes are still in use in practically the same form as originally described. Since their discovery no new process has been developed. It was claimed that heating rubber with metallic sulphides (such as antimony sulphide) constituted a new idea, but it was shown that this was merely a modification of Goodyear's method, and the vulcanization was due to the free sulphur which these sulphides contain.

The methods for vulcanizing may be classified as follows: By the hot process—(*a*) Heating with sulphur (press, steam, or hot air); (*b*) dipping in molten sulphur. By the cold process—(*a*) Dipping in a solution of sulphur chloride; (*b*) exposure of rubber to sulphur-chloride vapor.

One important difference between the hot and cold processes is that in the former the vulcanization proceeds throughout the entire mass, while in the latter the reaction occurs on the surface. The cold process can be used only with a very thin layer of rubber, such as is present in waterproof fabric, etc.

Mechanical goods are vulcanized by Goodyear's process, using either sulphur or metallic sulphides, or both. The other processes will therefore require no further comment at this time. Flat goods, such as belting, packing, etc., and various molded goods, are usually vulcanized in a steam-heated hydraulic press. Plied hose and insulated wire are vulcanized in steam. The vulcanization of fire hose and braided hose will be referred to later.

The degree of vulcanization will depend largely on the following factors: (1) Kind of crude rubber; (2) ratio of the percentages of rubber and sulphur; (3) method of heating (press, steam, air, etc.); (4) temperature; (5) time of heating; (6) size and shape of the article.

These factors are independent of one another, so that all of them must be considered in determining the proper conditions for vulcanizing in any particular instance.

(*h*) RUBBER HOSE.—The ordinary "plied" hose with rubber tube and cover is manufactured as follows:

(1) *Tubes and Covers.*—For low-grade water hose of small diameter it is usual to form the tubes by passing the rubber compound through a die which may be adjusted to produce a wall of any desired thickness. The rubber coming from the mixing rolls must be at a sufficiently high temperature to make it plastic, in which condition it is forced through the die by means of a worm. The operation is similar to that of a "soft-mud" brick machine, and the tube as it comes from the die is carried away on an endless belt. These tubes are placed on steel mandrels by a rather ingenious process, as follows:

The mandrel, which is about 52 feet long, is placed on an endless belt and held stationary. Powdered talc is blown into the tube to act as a lubricant and to prevent it from sticking to the mandrel during vulcanization. One end of the tube having been placed over the mandrel, air pressure is applied at the other end, sufficient to expand the tube slightly. The belt is now set in motion, and the tube as it is fed onto the belt floats over the mandrel on a cushion of air. In the case of high-grade hose and hose of large diameter the tube is made from a strip of sheet rubber, cut with a "skive" or tapering cut, which is wrapped over the mandrel by hand, the edges being lapped and pressed flat by means of a small hand roller.

In either case the cover is made from a strip of sheet rubber just wide enough to pass once around the hose and form a narrow lap.

To insure firm adhesion between the tube and canvas, the former is cleaned with gasoline preparatory to receiving the frictioned canvas.

(2) *"Making Up" the Hose.*—Water hose of small diameter is usually wrapped by machinery, consisting of three rolls about 2 inches in diameter and slightly more than 50 feet long. The two bottom rolls lie in the same horizontal plane, and the top roll, which is just above and between the other two, may be raised while the mandrel carrying the tube to be wrapped is being placed on the bottom rolls. The top roll is now lowered onto the tube, which is held firmly between the three rolls. A rotary motion imparted to the rolls causes the tube to revolve, and the canvas and rubber cover are wrapped on in a few seconds. This method has the advantage of consuming very little time, but unfortunately it is not applicable to the construction of best-quality hose, which is made up by hand with the assistance of small rollers having a concave face. The rollers are run up and down the hose and serve to press each ply of frictioned canvas onto the next.

Before going to the vulcanizer the hose is wrapped with cloth. First, a long strip is wrapped lengthwise on the hose, and over this a narrow strip is wrapped spirally. This is done very rapidly by causing the hose to revolve in roller bearings while the narrow strip of cloth is held under tension and guided by hand. The operation requires only a few minutes.

(3) *Vulcanizing.*—The vulcanizer consists of a long cylinder, provided with steam and drip connections and a pressure gauge. The pressure and time necessary for vulcanization depend upon the composition of the rubber compound, the thickness, and the use for which the hose is intended. After vulcanization the wrapping cloth is stripped off, and the hose is removed from the mandrel by means of compressed air in the same way that the tube was put on. The couplings are now put on and the hose is ready for shipment.

(4) *Cotton Rubber-Lined Hose.*—In the manufacture of woven cotton hose with rubber lining, the tube is made in the usual way and partially vulcanized, in order that it may develop sufficient strength to be drawn through the cover. A long slender rod is passed through the cover, carrying with it a stout cord. This cord is attached to the end of the rubber tube and the rod is withdrawn. The cord is now drawn through the cover, bringing the tube with it, the tube having been coated with rubber cement. The hose is now filled with steam under pressure, which expands the tube, thus forcing the cement well into the meshes of the woven cover and at the same time vulcanizing the rubber.

(5) *Braided Hose with Rubber Tube and Cover.*—A form of braided hose which is claimed to have, and appears to have, decided merit is made as follows:

The rubber tube passes first through a bath of cement and then to the braiding machine, where the first ply of fabric is braided over the fresh cement. This operation is repeated until the desired number of plies have been formed, when the rubber cover is put on and the hose is vulcanized in a mold. While being vulcanized the hose is subjected to air pressure from within, which forces the rubber well into the meshes of the loosely braided fabric.

(*i*) RUBBER BELTING.—Duck for rubber belting is passed over steam-heated rolls to remove the moisture, and frictioned as described in connection with the manufacture of rubber hose.

The frictioned duck is cut lengthwise into strips, the width of which depends not only upon the size of belt, but also upon the method of manufacture, which is not the same in all factories. These strips are cut by passing the canvas over a drum against which knives are held at points necessary to produce the desired widths.

One method is to make the inner plies of the belt with strips which are equal in width to that of the belt. These strips, stacked one above the other, are placed in the center of a strip of double the width, and in this position they are drawn through an opening with flared edges, which folds the bottom strip over the others and forms a butt joint on the top face of the belt. The belt then passes between rolls, which press the plies firmly together and at the same time lay and press a narrow strip of rubber over the joint. When the belt is to have a rubber cover, as is usually the case, this is calendered onto the outside ply or layer of the canvas before it is put on the belt. Some of the most expensive belts, however, are made without a rubber cover.

Another method is to cut each strip of canvas twice as wide as the belt. The first strip is folded upon itself, as described above, so that its edges form a butt joint. This folded strip is placed with its joint down upon the next strip, which is in turn folded to form a butt joint on the back of the first strip. In this way the belt is built up with the desired number of plies, the last joint being covered with a narrow strip of rubber, which is rolled flush with the surface. The belt is now ready to be vulcanized.

In this process the belt is stretched and held under heavy pressure between the steam-heated faces of a long hydraulic press. This drives the friction into the pores of the duck and vulcanizes the belt throughout.

As regards the advantage of using a high-grade rubber cover for belting, the consensus of opinion seems to be that the expense thus incurred, except in the case of conveyor belting, had better be devoted to increasing the quality of friction between the plies of canvas.

(*j*) INSULATED WIRE.—The first stage in the preparation of insulated cables is the drawing of the wire. The copper is drawn through a series of hardened dies, each one slightly smaller than the preceding one, until the desired size is obtained. The wire is cleaned by passing it through a bath of dilute nitric acid, and then coated with tin by running through a bath of melted tin. The purpose of this coating is to protect the copper from the action of the sulphur in the rubber.

The wire is then coated in one of two ways: The rubber may be "squirted" on the wire through a machine resembling the tubing machine used in making hose, etc., or it may be calendered into thin sheets, the latter cut into strips and wound around the wire.

After vulcanization the wire is sometimes protected from injury by a covering of braid. If waterproofing is desired, the braided wire is dipped in melted tar and paraffin.

(*k*) RUBBER TUBING.—Rubber tubing, for which there is a very large demand, is made either with a tubing machine, as described on page 14, or from calendered sheet. Compounded tubing, which is most extensively used for general purposes, is made by the former method. Dies and cores of different sizes are provided, which may be interchanged to produce any diameter and thickness of wall within the machine's capacity.

Pure-gum tubing is usually made from calendered sheet by wrapping a strip of the gum around a rod of suitable diameter. It is sometimes made with a tubing machine, but its production by this means is rather difficult and requires careful supervision.

Tubing is vulcanized in open steam. In preparation for this process the lower grades are covered with talc to prevent adhesion of the walls, while the better grades, which become very soft during vulcanization, are wrapped on a mandrel, as described on page 15, in connection with the manufacture of plied hose.

(*l*) MOLDED RUBBER GOODS.—Molded rubber goods cover such a wide field and are produced in such a great variety of forms that no attempt can be made here to describe in detail the manufacture of individual articles. Mechanical goods such as pump valves, heels and soles, floor tile, etc., are generally cut or punched from sheeted stock and vulcanized in molds between the steam-heated faces of a hydraulic press. Articles of irregular shape are built up in the molds.

Solid tires are "squirted" through a tubing machine and vulcanized in steam-jacketed molds. Pneumatic tires are vulcanized in molds under pressure, the molds being surrounded by steam. In the case of wrapped-tread tires the mold does not completely inclose the tire, but merely clamps it on the sides as far as the tread. The tire thus clamped on the sides is well wrapped with cloth strips before vulcanization.

III. PHYSICAL TESTING OF RUBBER

Rubber testing in the present stage of its development is not susceptible of very great refinement as regards measurement. The nature of the material is such that refinement seems of less importance than uniformity of methods, which is absolutely essential where the work of different laboratories is to be compared. A more general interest in this matter would result in a substantial benefit not only to reputable manufacturers and large consumers, but also to the public.

1. PHYSICAL TESTS MOST COMMONLY EMPLOYED

The different properties that have been found desirable in rubber intended for various purposes have naturally given rise to numerous tests, of which the most widely applicable are the various tension tests. These tests in various forms are used to determine the more important physical properties, such as tensile strength, ultimate elongation, elasticity, and reduction in tension when stretched to a definite elongation.

In the case of such materials as rubber hose and rubber belting, which are built up with layers of duck cemented or frictioned together with rubber, it is customary to determine the friction or adhesion between the plies of duck as well as the quality of rubber. It is also usual to subject hose (particularly fire hose and air hose) to a hydraulic-pressure test, in order to detect any imperfections in materials or workmanship.

An important test in the case of steam hose consists in passing steam at about 50 pounds pressure through a short length of the hose, in order to determine if the rubber is of suitable composition to withstand the effects of service conditions. This test usually lasts for about six days, the steam being turned off at night to allow the rubber to cool. A decided hardening or softening of the rubber, or a large decrease in the value of friction, as a result of steaming, is an indication of inferior quality.

No absolutely reliable test (other than an actual service test) has been devised for rubber steam packing, but in many cases valuable information may be obtained by clamping a piece of the packing between metal plates and subjecting it to the action of steam at a pressure equal to or slightly above that under which it is to be used. A more satisfactory method is to clamp the packing in the form of a gasket between pipe flanges and apply the desired steam pressure from within. The test should last several days, the steam being turned off at night to see if the joint has a tendency to leak as a result of the cooling effect. This, however, practically constitutes a service test.

The testing of tires, or rather the materials used in their construction, is done almost exclusively by manufacturers. Manifestly, it would be too expensive for the consumer, or even the dealer, to sacrifice whole tires for the purpose of securing test pieces. The more progressive manufacturers, however, realize that money expended in thorough and careful testing is more than justified by the increase in efficiency of their production.

The tests which have been outlined above will, in the majority of cases, enable one to form a fairly accurate judgment as to the quality of rubber. It sometimes happens, however, that rubber which shows evidence of good quality just after vulcanization is found to deteriorate rapidly with age. This has led to a number of proposed accelerated tests, whose common object is to hasten by artificial means the deteriorating effect of age. A test of this nature, which merits further investigation, consists in the application of dry heat. The effect of dry heat at 160° F. on the tensile strength and ultimate elongation of five rubber compounds is shown in Figs. 2 and 3. Figs. 4 and 5 show the effect of age on the same material.

(*a*) TENSILE STRENGTH AND ULTIMATE ELONGATION.—(1) *Separating Rubber from Fabric.*—When the material is made up with layers of fabric, as in the case of rubber hose, the first step in preparing specimens for the tension test is to separate the rubber from the fabric. Unless the frictioning is very poor, this will necessitate the use of a solvent. If there is more than one layer of fabric, the easiest way is to remove the first layer along with the rubber. The rubber is then separated from the adjoining layer of fabric, using gasoline blown from a wash bottle. Narrow strips are more easily handled than larger pieces, and there is less danger of injuring the rubber. Great pains should be taken during this operation, because any flaw or local imperfection will seriously vitiate the results. The rubber should be allowed to rest for several hours, in order that it may recover from the stretching it has received and that the gasoline may thoroughly evaporate.

(2) *Emery Wheel for Grinding the Surface of Rubber.*—The strips thus removed retain the impression of the fabric from which they

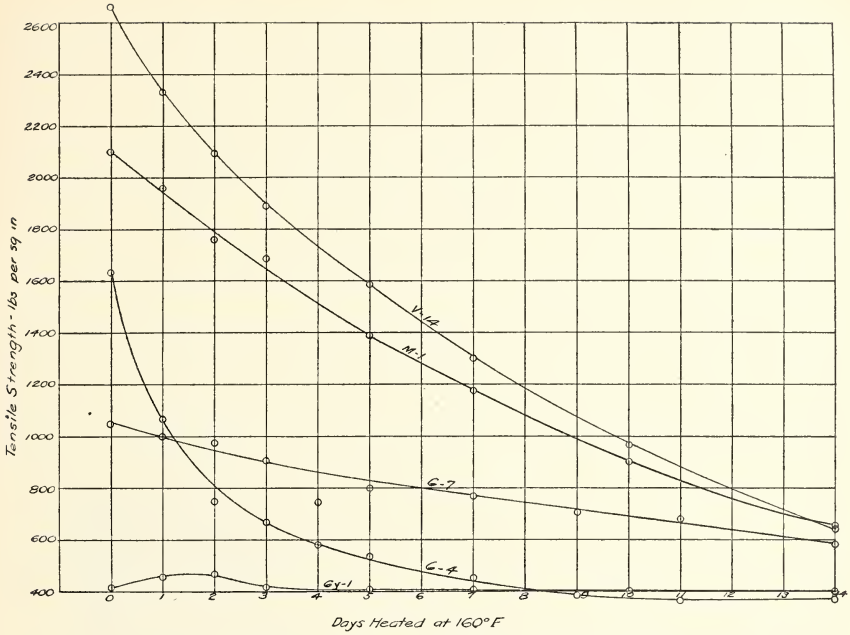


FIG. 2.—*Effect of dry heat on the tensile strength of rubber.*

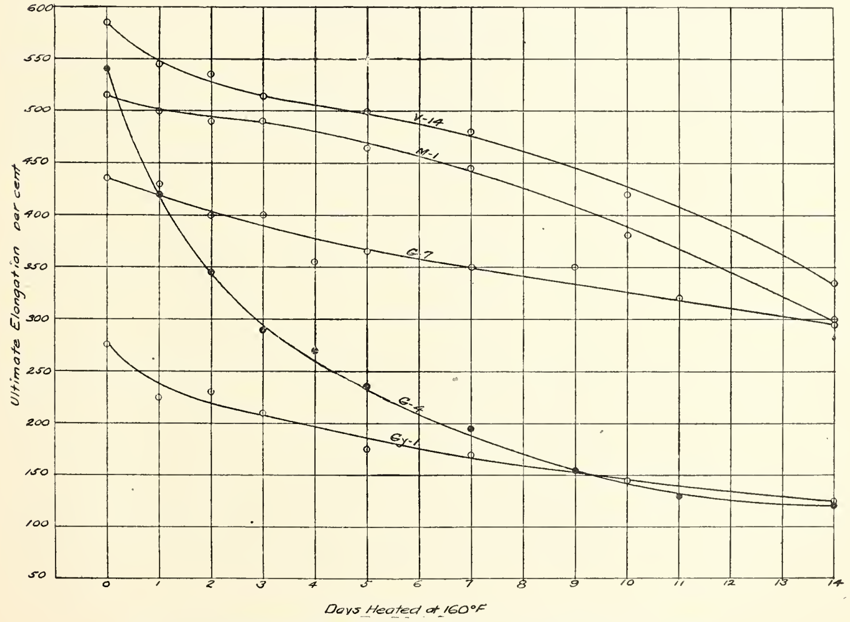


FIG. 3.—*Effect of dry heat on the ultimate elongation of rubber*

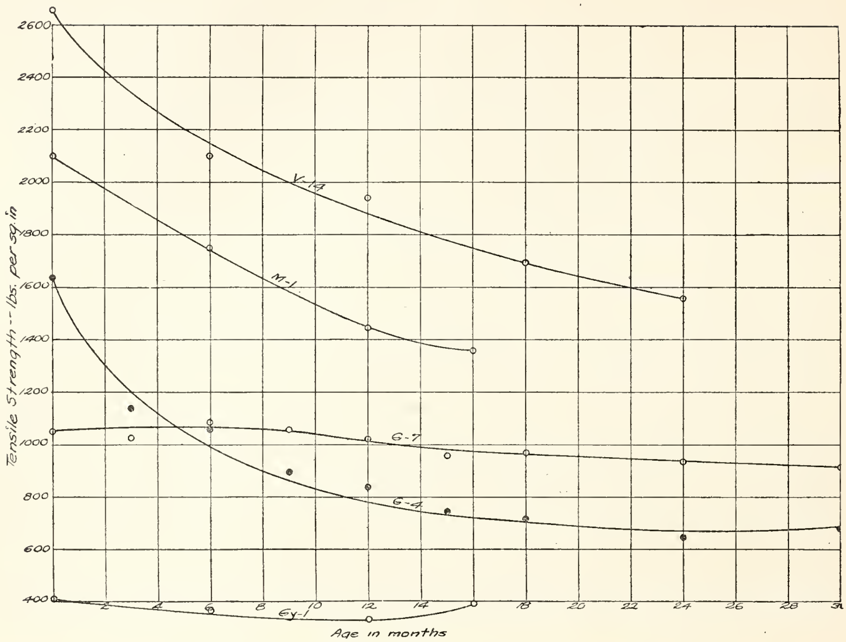


FIG. 4.—*Effect of age on the tensile strength of rubber*

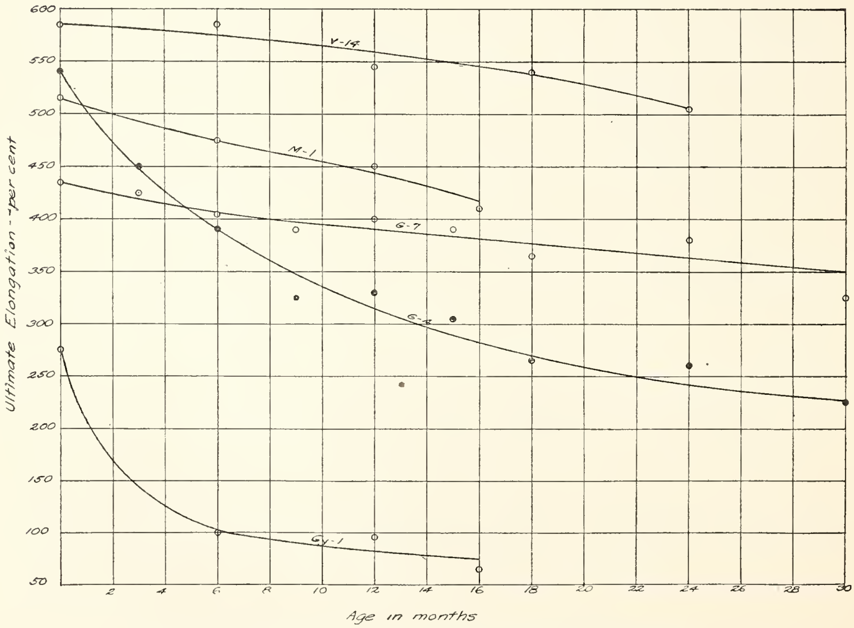


FIG. 5.—*Effect of age on the ultimate elongation of rubber*

have been separated, and it is necessary to grind the surface smooth in order to measure accurately the thickness of the test pieces. The emery wheel shown in Fig. 6 was designed at this Bureau to accomplish this purpose, and has proven a very convenient and satisfactory arrangement. The wheel is operated by a one-tenth-horsepower motor. The rubber to be buffed is clamped as shown to a carriage, which is moved back and forth under the 5 by 1¼ inch emery wheel (No. 60), running at about 3000 revolutions per minute. The central portion of the carriage just under the rubber is slightly raised, by which means it has been found that the operation is more easily performed and with less danger of injury to the rubber. An adjusting thumbscrew serves to lower the wheel by very small amounts as the buffing proceeds. Shields are provided to keep the fine particles of rubber off of the guide. The starting box, though not necessary, is desirable in bringing the wheel gradually up to full speed.

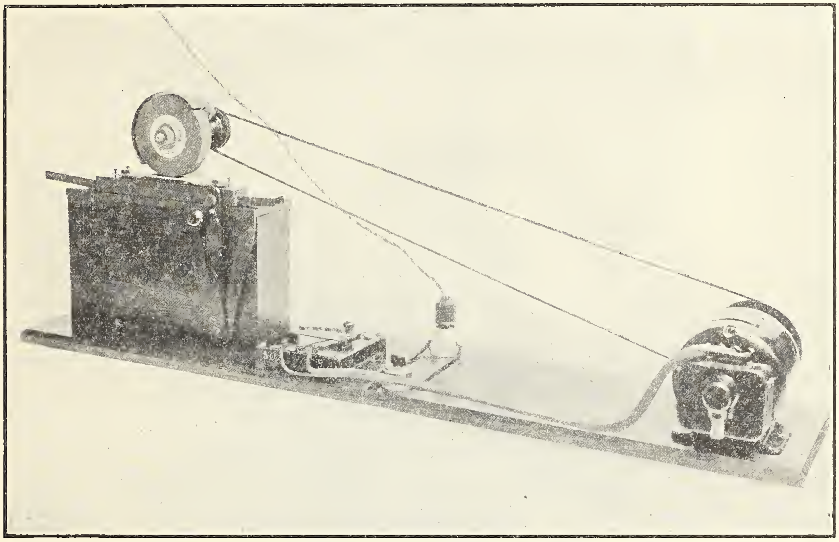


Fig. 6.—*Emery wheel for grinding the surface of rubber test pieces*

(3) *Form and Preparation of Test Pieces.*—Test pieces are cut with a metal die, which not only saves much time, but also insures uniform width, which it is impossible to obtain if the specimens

are cut by hand. An arbor press, Fig. 7, is perhaps the most convenient and satisfactory means of forcing the die through the rubber, although many prefer to cut the test pieces by striking the die with a mallet. The operation is facilitated by wetting the cutting edges of the die, and the rubber should rest on a smooth

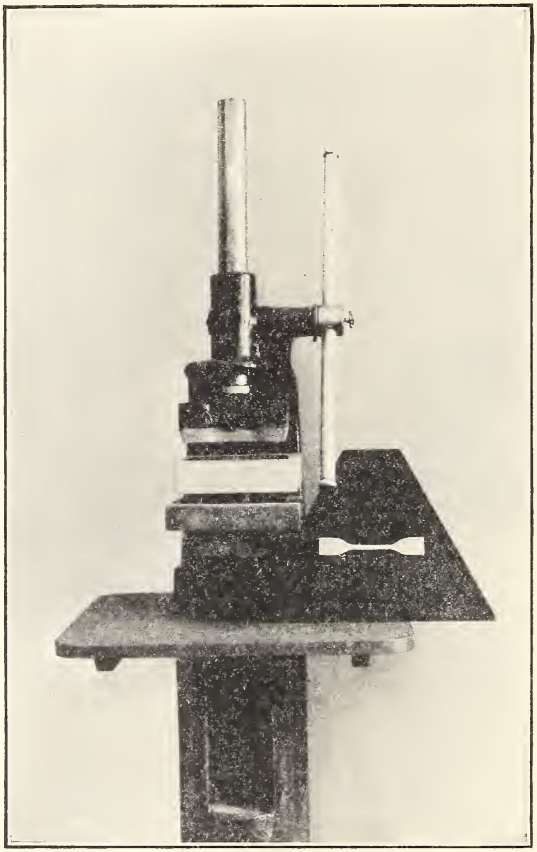


Fig. 7.—*Arbor press and die for cutting rubber test pieces*

and slightly yielding surface which will not injure the cutting edges. A piece of leather is suitable for the purpose. The central portion of the test piece is straight, and the ends are gradually enlarged to prevent tearing in the grips of the testing machine. The width of the contracted section is usually made either one-fourth inch or one-half inch. Fig. 8 gives the dimensions of test pieces which have been found to give satisfactory results. The one-fourth-inch test piece is to be preferred for general use, for the reason that there is a less tendency for the rubber to tear in the grips or across the shoulder where the cross section changes.

Parallel lines are placed on the specimens, and by means of these gauge marks elongation and permanent extension are measured. A stamp consisting of parallel steel blades enables one to mark very fine lines with ink, without cutting the rubber, and in this way much time is saved and the chance of error very much reduced.

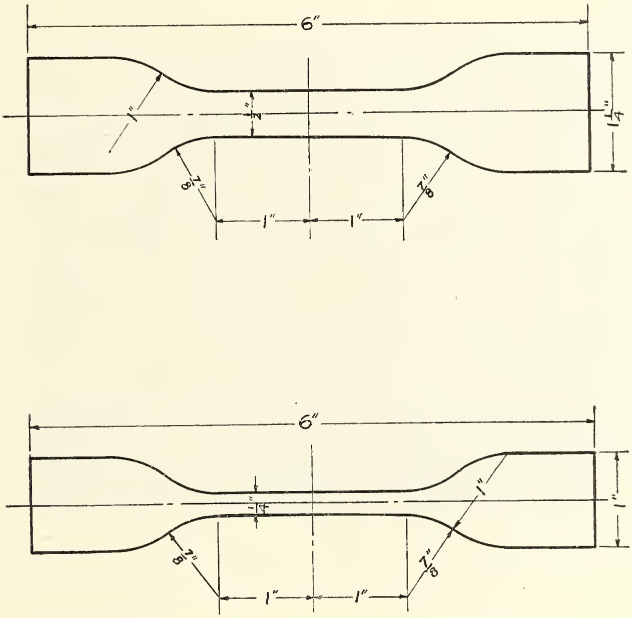


Fig. 8.—*One-fourth and one-half inch test pieces with enlarged ends*

In testing pure gum or compounds containing a large percentage of rubber, it is not practicable with a machine of convenient length to break test pieces having a gauge length of 2 inches. In such cases shorter test pieces, having a gauge length of 1 inch, are used. Test pieces in the form of a ring will be referred to later on page 42.

(4) *Measuring the Thickness of Rubber.*—There is a special form of micrometer caliper (Fig. 9, A) provided with enlarged contact surfaces and ratchet stop, which is well suited for measuring the thickness of rubber and textile materials. The ratchet stop makes it possible to measure each specimen under the same pressure and thus adds to the uniformity of results. A spring micrometer (Fig. 9, B) is exceedingly convenient and is very easily read.

(5) *Grips for Holding Test Pieces.*—In testing rubber one of the greatest difficulties has been to grip the test piece in such a way as to prevent slipping, without at the same time injuring the rubber. Even a very small scratch on the surface of a rubber test piece is often sufficient to cause failure at that point.

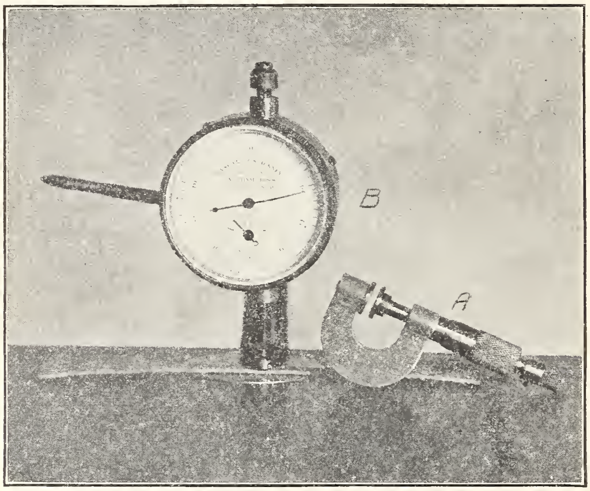


Fig. 9.—*Instruments for measuring the thickness of rubber*

A, Micrometer caliper; B, spring micrometer

In order to prevent slipping of the test piece as its section is gradually reduced under increasing tension, it has been found advisable to provide means for automatically tightening the grip. This is conveniently accomplished by using a number of thin cylindrical disks mounted eccentrically on a pin (Fig. 10, A), which act independently, thus producing a uniform pressure over the gripping surface and preventing any uneven slipping.

When it is desired to test specimens of circular form, as in the case of rubber bands or washers, grips of the design shown in Fig. 10, B, may be used. Each grip consists of two rollers mounted on ball bearings. The action of these rollers is such that as tension is applied they rotate in opposite directions, thus tending to equalize the stress around the circumference of the test piece.

(6) *Testing Machines.*—The machine shown in Figs. 11, 12, and 13 is used for determining the tensile strength and ultimate elongation. The dynamometer 1 (Fig. 11), having a capacity of 125 pounds and graduated to one-fourth pound, is attached to the upper end of column 2, which is slotted to receive the rack 3, carrying the eccentric grip 4 at its upper end. The machine is operated by a $\frac{1}{12}$-horsepower motor, which is belted to the stepped pulley 5. A worm on the pulley shaft drives a worm wheel which is geared to a spur (not shown) inside of column 2. The eccentric grip 6 (Fig. 12) is attached to the dynamometer through pin connections 7 and 8. The plate 9 serves to prevent recoil of the springs when a specimen is broken, and acts in the following manner: The rod 10, which is rigidly attached to column 2, passes with very little clearance through a hole in the back of plate 9. The front of plate 9 is slotted to receive the rod 11, and is supported by the shoulder 12. As tension is applied to the specimen,

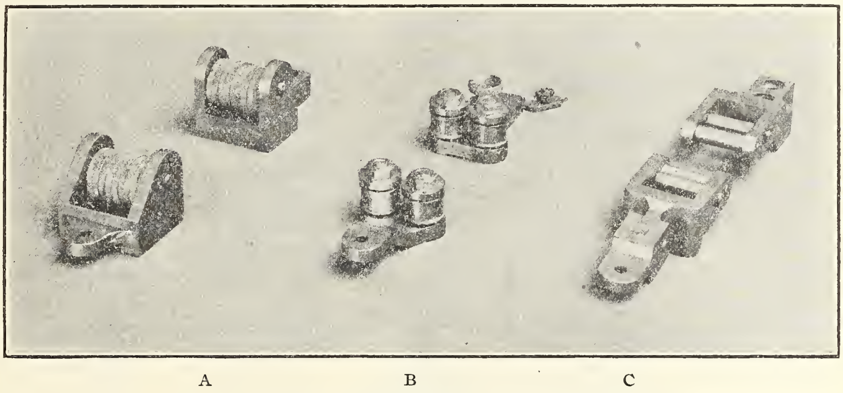


FIG. 10.—*Grips used in making tensile tests of rubber*

A, Eccentric disks which tighten automatically as the tension increases; B, spools with ball bearings for testing ring-shaped specimens; C, grips used for testing the rubber insulation of wire

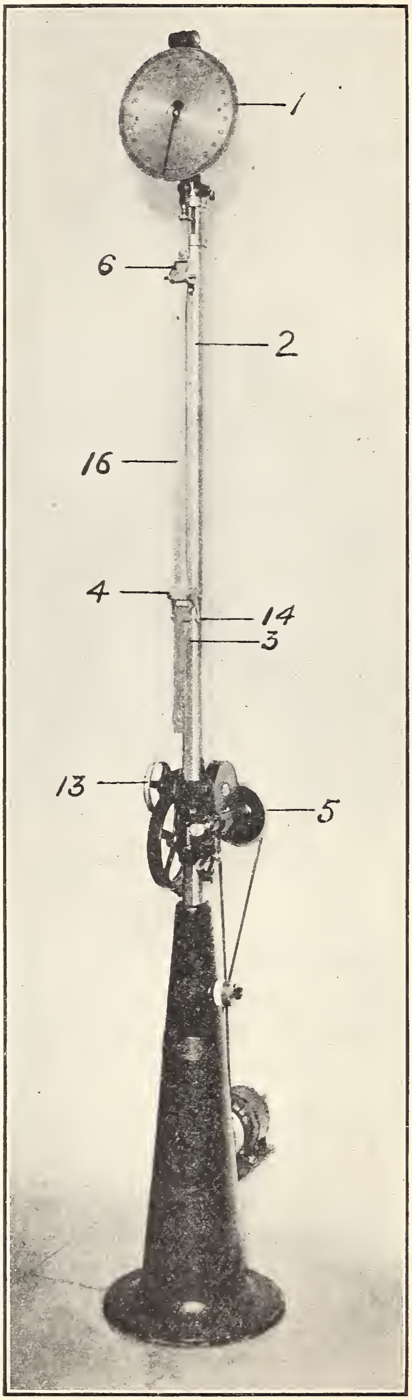


Fig. 11.—*Motor-driven machine for testing the tensile strength of rubber*

plate 9 is free to follow the shoulder 12, and passes down over the rod 10, but when the specimen breaks the upward pressure of the shoulder 12 causes the plate to bind on the rod 10, thus holding the springs under the maximum tension. The dynamometer is so constructed that the pointer remains at the maximum load when a specimen breaks. The load having been recorded, the upper grip is pulled downward (by means of the hand wheel 13, and hooks 14, if necessary, Fig. 11) to relieve the pressure of the shoulder 12 against plate 9, and at the same time the rear end of the plate is raised to release the rod 10. The tension of the springs may now be relieved by allowing the grip to rise, and the pointer is returned to zero.

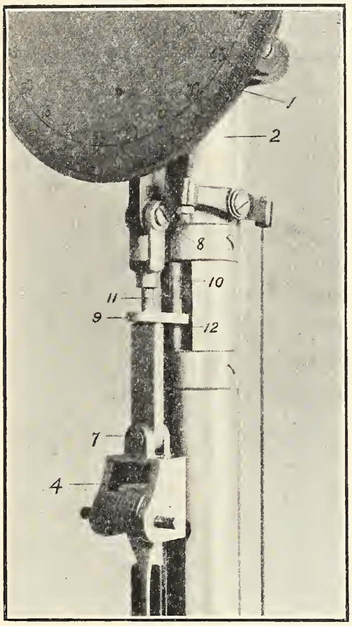


Fig. 12.—*Detail of upper portion of machine shown in Fig. 11*

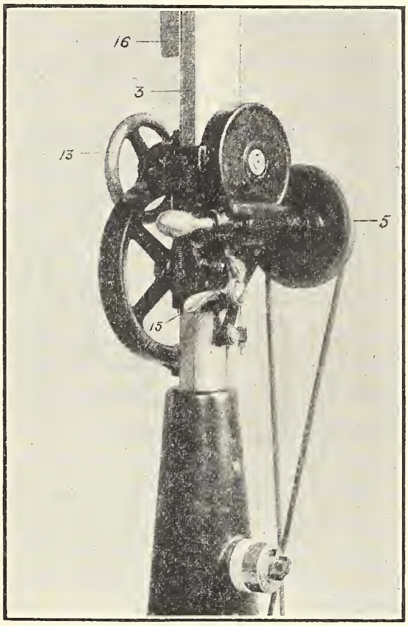


Fig. 13.—*Detail of lower portion of machine shown in Fig. 11*

At the end of a test the worm and gear are disengaged by means of the spring clutch 15 (Fig. 13), and the rack is rapidly raised by hand to its initial position.

The stepped pulleys provide for different speeds to meet the requirements of experimental work.

Elongation between gauge marks on the specimen may be measured on the scale 16, attached to column 2, but to do this requires the services of two operators. A simpler and equally accurate method is as follows: A wooden scale graduated to one-tenth inch, as shown in Fig. 14, is held in a slightly inclined position at the back of the test piece with its lower end pressed lightly against the rubber just back of the lower gauge mark. As the rubber is stretched the eye follows the scale just back of the upper gauge mark. With a little practice the elongation at break may be measured with a fair degree of accuracy.

The Schopper machine, illustrated in Fig. 15, is worked by hydraulic power, its operation, briefly stated, being as follows: The rubber test ring is placed over the spools, and the lower spool is geared to the rack in such a way that it is caused to revolve during a test. This motion is transmitted to the top spool by the rubber test ring, the object of rotating the spools being to equalize the tension at all parts of the specimen. As the tension is increased the weighted lever, to the short arm of which the top spool is attached, is gradually deflected. When the test ring is broken, the lever is held at the point of maximum load by means of a set of pawls, the breaking load being read from the curved scale and the elongation being indicated by the vertical scale just opposite the test ring.

Fig. 16 shows a motor-driven machine of 15 pounds capacity which was designed for testing rubber bands. The load is applied through the steel tape 1, at the end of which is the grip 2, carrying spools 4, similar to those shown in Fig. 10, B. The graduated steel tape 3, attached to grip 2, with its zero point coinciding with the center of the spools 4, passes up behind the test specimen and through the column 5 to a reel just behind the spring balance. When the specimen breaks its elongation is determined by the distance between the centers of spools as shown by the tape 3. The plate 6 holds the springs under the maximum tension in a way already explained in connection with Fig. 12. Stepped pulleys provide for different speeds. When a specimen has been broken, the worm and gear are disengaged by means of the lever 7, and the bottom spools are raised by hand to their initial position.

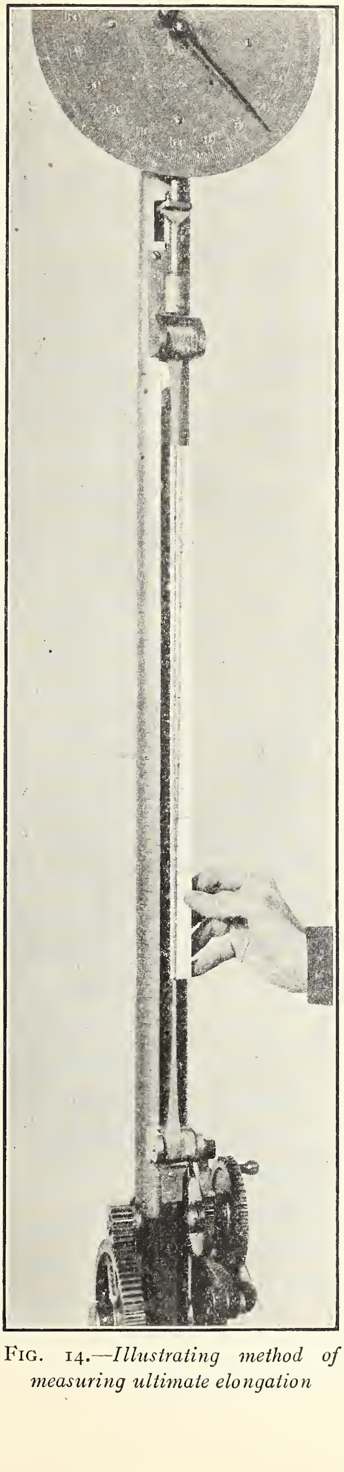


Fig. 14.—*Illustrating method of measuring ultimate elongation*

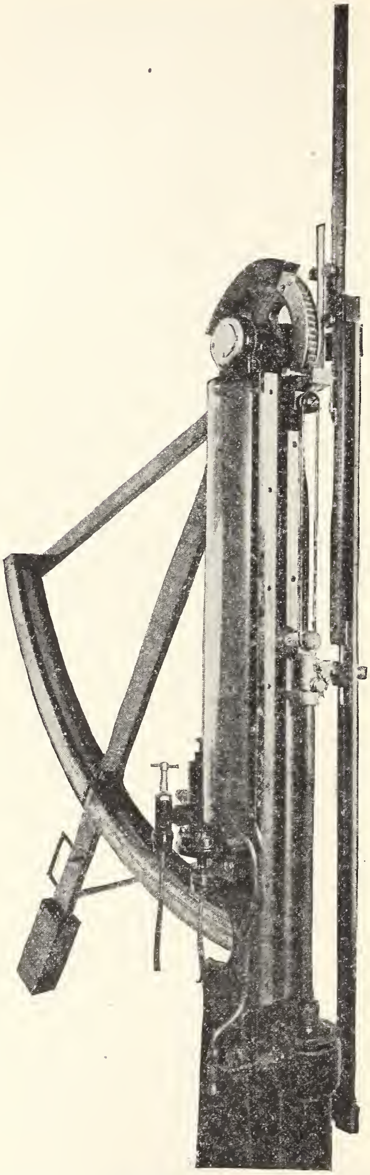


FIG. 15.—"*Schopper*" *machine for testing the tensile strength of rubber*

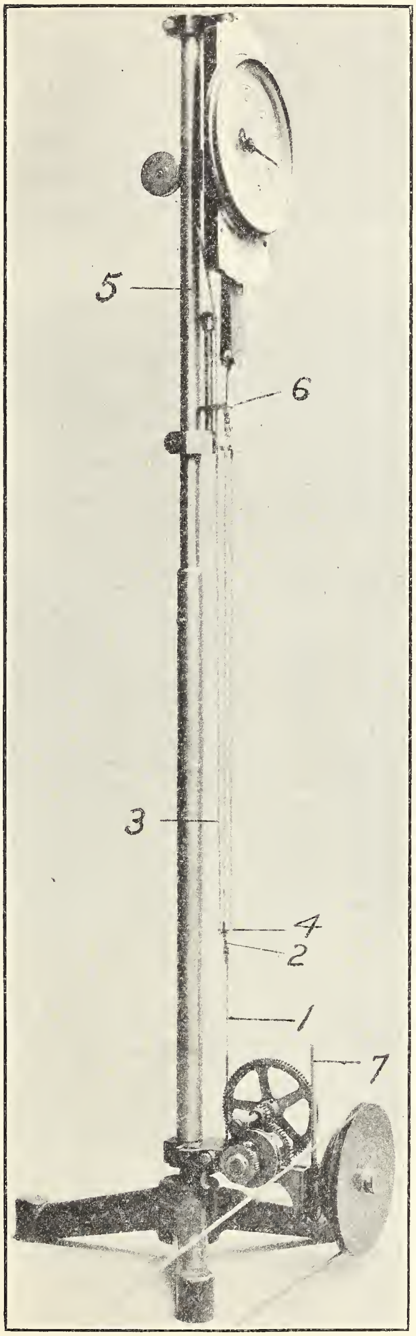


FIG. 16.—*Motor-driven machine for testing rubber bands*

This machine is also provided with eccentric grips which are used for testing straight specimens of low tensile strength.

(*b*) ELASTICITY OR "SET."—"Set" or "recovery," as applied to rubber, is in a way synonymous with elasticity, and is measured by the extent to which the material returns to its original length after having been stretched. The term "set," as commonly employed, refers to the extension remaining after a specified interval of rest following a specified elongation for a given period of time. For example, if a test piece is stretched from 2 inches to 10 inches for 10 minutes and then released, and if its length measured after 10 minutes rest is 2.4 inches, the "set" under these conditions is 0.4 inch or 20 per cent.

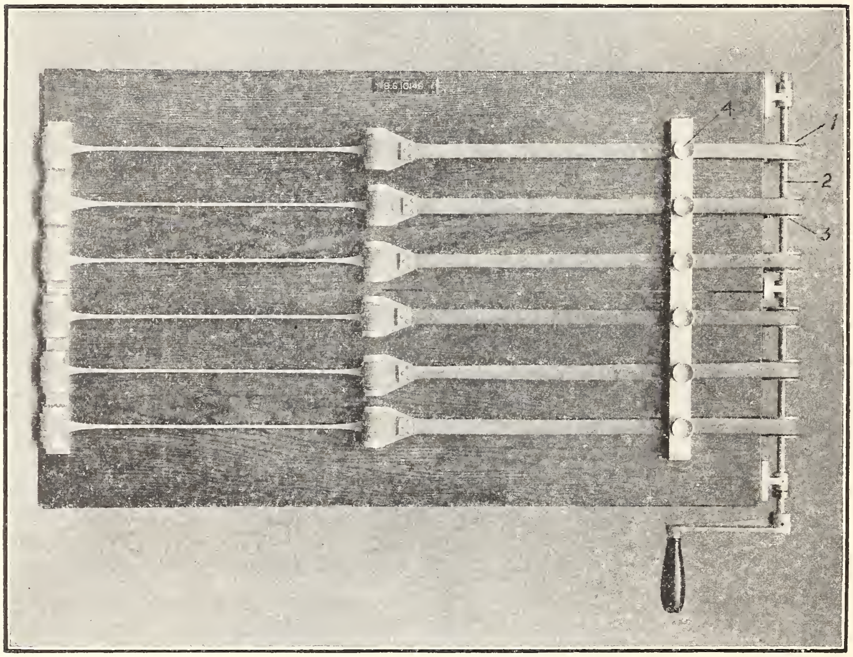


FIG. 17.—*Apparatus for stretching rubber to determine its elasticity*

(1) *Machine for Testing Elasticity or "Set."*—For merely stretching rubber to determine its elasticity or recovery after a definite elongation, without reference to the tension applied, the apparatus shown in Fig. 17 is used, in which six specimens may

be tested at once. The spools 1 are free to slide on the shaft 2, and are slotted to engage pins 3 (not shown), which act as clutches. The movable grips are attached to three-fourths inch strips of leather-belt lacing which pass through clamps 4 and then to the spools 1. The action of these clamps is similar to that of an ordinary letterpress, and, with a one-half inch by three-fourths inch bearing plate, a moderate twist of the knurled head is sufficient to prevent any slip of the belt lacing when under tension. The operation of the apparatus is as follows:

Six specimens being in the grips, one of the spools is moved along the shaft until it engages the corresponding pin, and the shaft is revolved until the desired elongation measured between gauge marks on the specimen is secured. The clamp is tightened to hold the specimen in this position, and the spool is shifted back so as to disengage the pin. The operation is repeated with each of the specimens in turn. Each specimen is released after a specified length of time (usually from 1 to 10 minutes) and after an equal interval of rest the permanent extension or set is measured.

(*c*) REDUCTION IN TENSION WHEN RUBBER IS HELD AT A DEFINITE ELONGATION.—When rubber is stretched in a testing machine the extension gradually increases with the applied tension, as is the case with other materials, but if the machine is stopped at any point so that the test piece is held fixed under a constant elongation, the tension in the test piece will gradually decrease.

The determination of this decrease in tension under specified conditions constitutes a test which is thought to be indicative of the quality of rubber and the extent of vulcanization.

(1) *Machine for Testing Reduction in Tension.*—The apparatus shown in Fig. 18, which has a capacity of four test pieces, is used in conducting this test. The spring balances are provided with live and dead pointers, which show the maximum tension as well as the tension at any time during the test. The balances have a capacity of 50 pounds, with 8-inch dials graduated to 0.2 pound. The lower grips are counterbalanced by weights, which are suspended from cords passing over pulleys just back of the spring

balances. In this way each grip is held in an accessible position and is prevented from falling should the specimen break.

(*d*) CONDITIONS AFFECTING THE RESULTS OF TENSION TESTS.—In the absence of uniform methods of testing, it is found that results obtained in different laboratories sometimes show marked discrepancies which are due to the varying conditions under which the tests are made.

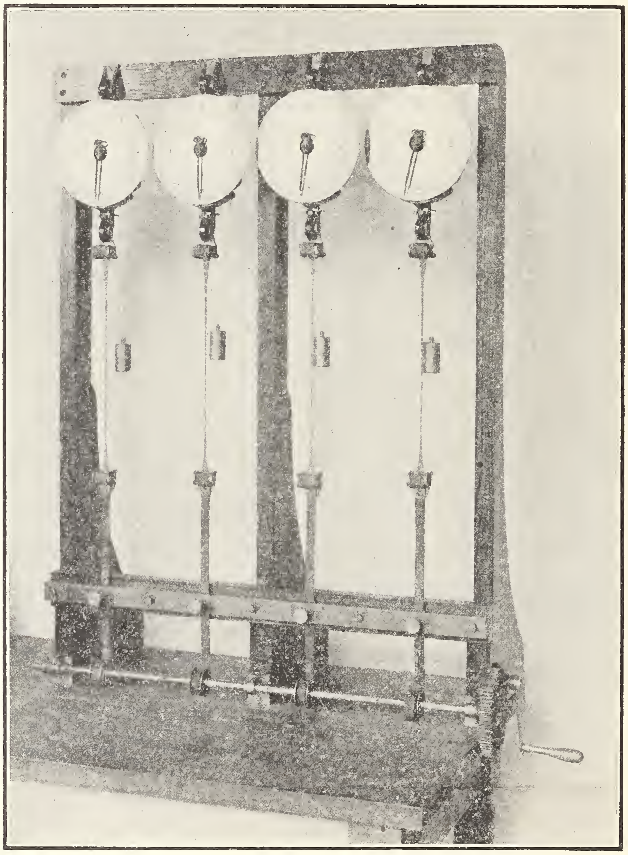


FIG. 18.—*Apparatus for determining the reduction in tension when rubber is stretched and held at a definite elongation*

(1) *Influence of Speed on Tensile Strength and Ultimate Elongation.*—The speed at which rubber is stretched probably affects the results to a less extent than is often supposed, though doubtless different rubbers are not equally affected.

Table 2 shows the results obtained in a comparative test of four compounds.

TABLE 2

Tensile Strength and Ultimate Elongation of Rubber when Stretched at the Rate of 5, 25, and 45 Inches per Minute

[Gauge length=2 inches.]

Reference	G-18			M-1			B-1			Gy-1		
Speed in inches per minute	5	25	45	5	25	45	5	25	45	5	25	45
Tensile strength (pounds per square inch)	2495	2690	2720	1900	1940	1970	375	430	465	340	390	430
Ultimate elongation (per cent)	605	635	635	465	500	490	340	360	375	105	115	120

These results would indicate a general tendency toward higher values for both tensile strength and ultimate elongation as the speed of stretching increases.

(2) *Influence of Temperature on Strength, Elongation, and "Recovery."*—It is generally recognized that the physical properties of rubber are affected by changes in temperature, though, of course, to a less extent after vulcanization than before.

Fig. 19 shows the results of tests at 50, 70, and 90 degrees Fahrenheit. In each case the room was maintained at the specified temperature for three hours before the tests were made. It will be noticed that the rubbers are not all affected to the same extent by equal differences in temperature, but there is a marked tendency in each case toward decreased strength, decreased set (increased elasticity), and increased elongation as the temperature is raised. It will be noted further that in nearly every case greater differences occur between 50 and 70 degrees than between 70 and 90 degrees.

The set in each case was measured after one minute stretch and one minute rest. Nos. 1 and 2 were stretched 350 per cent, Nos. 3 and 4, 300 per cent, and No. 6, 250 per cent.

(3) *Influence of Cross Section on Tensile Strength and Ultimate Elongation.*—Tensile strength and ultimate elongation are theoretically independent of sectional area, but, as in other materials,

there is a tendency for small test pieces to develop higher unit values than large ones. Complete data on this subject is not at hand, but it is thought that test pieces one-fourth inch and one-half inch wide will show, in general, but little difference in ultimate elongation, but an appreciable difference in tensile strength of high-grade compounds.

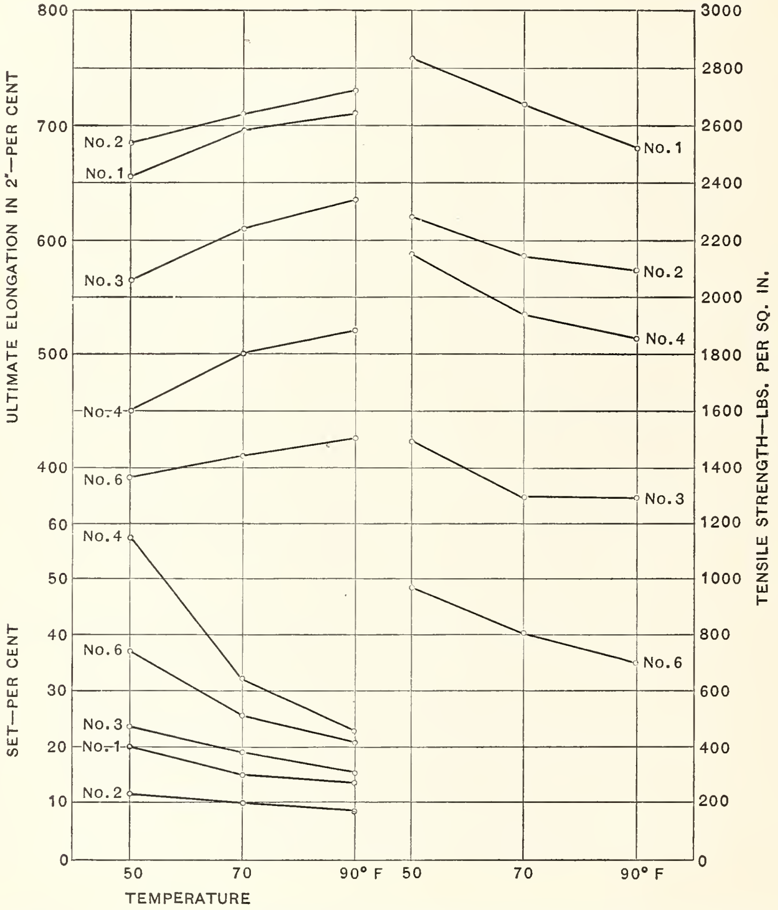


Fig. 19.—*Influence of temperature on the elasticity, tensile strength, and ultimate elongation of rubber*

Comparative results obtained with test pieces one-fourth and one-half inch wide are shown in Table 3. These rubbers represent commercial compounds. The test pieces were cut from the tubes and covers of plied hose, and the impression left by the fabric was carefully removed with the emery wheel shown in Fig. 6.

TABLE 3

Influence of Cross Section upon the Tensile Strength and Ultimate Elongation of Rubber

Rubber No.	M-4 cover		M-3 tube		G-19 tube		G-19 cover		M-5 tube	
Width of specimens (inches)	One-fourth	One-half	One-fourth	One-half	One-fourth	One-half	One-fourth	One-half	One-fourth	One-half
Tensile strength (pounds per square inch)	1565	1455	2160	1955	1025	955	735	690	2490	2060
Ultimate elongation in 2 inches (per cent)	525	515	580	570	350	340	255	250	615	575

(4) *Influence of the Direction in which Specimens are Cut on Strength, Elongation, and "Recovery."*—The tensile properties of sheet rubber are not the same in all directions, as will be shown later in connection with comparative tests of straight and ring-shaped test pieces. There is a tendency for specimens cut longitudinally or in the direction in which the rubber has been rolled through the calender to show greater strength and (at least for the better grades of rubber) less elongation than specimens cut transversely or across the sheet. The recovery, however, is greater in the transverse direction. Table 4 illustrates this.

TABLE 4

Showing the Relative Strength, Elongation, and "Recovery" of Rubber when Tested in the Longitudinal and Transverse Directions

Rubber No.	1	2	3	4	5	6
Tensile strength [1] (pounds per square inch):						
Longitudinal	2730	2070	1200	1850	690	880
Transverse	2575	2030	1260	1700	510	690
Ultimate elongation (per cent):						
Longitudinal	630	640	480	410	320	315
Transverse	640	670	555	460	280	315
Set [1] after 300 per cent elongation for 1 minute with 1 minute rest (per cent):						
Longitudinal	11.2	6.0	22.1	34.0	....	34.3
Transverse	7.3	5.0	16.3	24.0	....	25.9

[1] The set and tensile strength were determined with different test pieces.

No. 3 shows slightly greater strength transversely and No. 5 greater elongation longitudinally, while No. 6 shows the same elongation in each direction. The exception noted in No. 3 is attributed to experimental errors or to small defects in the specimens which escaped detection. It may be, however, that low-grade rubbers, such as Nos. 5 and 6, are not more extensible transversely than longitudinally. Further tests are necessary to determine this point.

(5) *Influence of "Backing" on the Tensile Strength and "Recovery" of Hose Lining.*—In the case of cotton rubber-lined hose the "backing" which is used to cement the lining to the fabric, if not removed, affects to a greater or less extent the values obtained for tensile strength and "set" or "recovery."

If the backing has an ultimate elongation greater than that of the lining, it must necessarily increase the tensile strength which is figured from the breaking load and the measured cross section of the rubber lining. The observed value for "set" or "recovery," which is obtained as described on page 34, is greater or less than the true value, according as the lining is more or less elastic than the backing. If the elasticity of the backing differs very much from that of the lining, it will be found that the broken test pieces have a tendency to curl up like a watch spring, with the backing on the inside or outside according as its elasticity is greater or less than that of the lining. It is customary to test hose linings with the backing removed.

In Table 5 are recorded the results of tests that were made to determine the effect of backing on the tensile properties of hose linings. For these tests the backing was removed with the emery wheel shown in Fig. 6. Differences in the values of tensile strength in lines A and B may be attributed partly to errors in measuring the thickness of the specimens that were tested without removing the backing. In the case of No. 1, however, it is thought that the thickness was determined without appreciable error. The adhesion between tube and backing being weak, it was possible to separate the two by hand, and the eight specimens thus secured showed a maximum variation in thickness of only 0''.003. The average thickness was used in computing the strength of specimens tested with backing (line A). It is seen that in this case the backing very materially increased the strength of the test pieces.

TABLE 5

Effect of Backing on the Tensile Properties of Hose Linings

Reference No.	([2])	1	2	3	4	5	6	7	8
Set after elongation and release (per cent)	A	[3] 24.5	[3] 17.5	[3] 17.5	[3] 20.5	[3] 24.0	[4] 20.5	[3] 21.0	[4] 21.5
	B	[3] 23.0	[3] 18.5	[3] 19.0	[3] 19.0	[3] 23.5	[4] 22.5	[3] 17.5	[4] 20.5
Tensile strength (pounds per square inch)	A	3080	3015	3025	2705	2795	2555	2095	1190
	B	2535	2790	2615	2720	2300	2410	2335	1190
Ultimate elongation (per cent)	A	590	625	645	650	580	535	550	535
	B	575	635	610	645	585	540	590	535

[2] A, Tested without removing backing: B, Tested with backing removed.

[3] Measured after 400 per cent elongation for 10 minutes, with 10 minutes rest.

[4] Measured after 350 per cent elongation for 10 minutes, with 10 minutes rest.

(6) *Influence of Previous Stretching on Strength, Elongation, and "Recovery."*—Test pieces that have been used to determine set usually show greater strength and ultimate elongation than are obtained with test pieces that have not been previously stretched.

Table 6 gives the strength and ultimate elongation obtained in testing six samples of rubber, first, with a single stretch, and second, by repeated stretching, beginning with 200 per cent and increasing each stretch by 100 per cent until failure.

TABLE 6

The Influence of Repeated Stretching on Tensile Strength and Ultimate Elongation

Rubber No.	1	2	3	4	5	6
Tensile strength (pounds per square inch):						
Single stretch	2470	1740	990	1710	750	930
Repeated stretch	2610	1960	1180	1790	790	920
Ultimate elongation (per cent):						
Single stretch	645	665	510	460	430	375
Repeated stretch	765	780	645	555	440	465

In testing rubber as described above, it is found that if during the latter part of the test the increments in extension for successive stretches are small (say 25 per cent of the original length), a point is reached where the rubber breaks down, and beyond which it fails on a subsequent stretch at a tension less than the maximum which it has already developed.

The recovery after a definite elongation is usually greater if the rubber has been previously stretched than if determined in the usual way. This is illustrated by the results shown in Table 7, in which the columns marked "Repeated stretch" show the set after repeated stretching, beginning with 100 per cent and increasing 100 per cent for each subsequent stretch. The results in columns marked "Single stretch" were obtained in the usual way, each specimen being stretched but once. In each case the set was measured from the original gauge marks, after one minute stretch and one minute rest, the tabulated results being the average of the values obtained in testing a number of specimens.

TABLE 7

The Influence of Repeated Stretching on the "Recovery" of Rubber

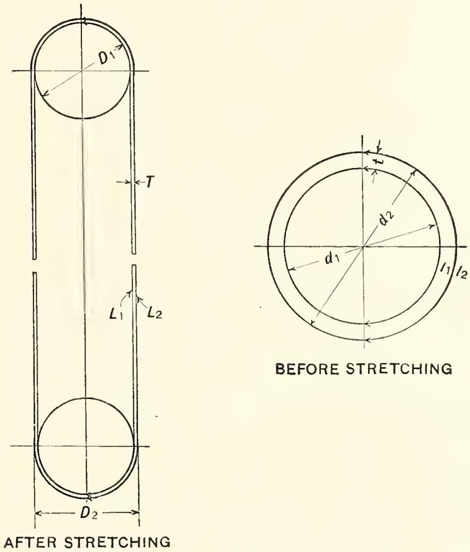
No.	Method of testing	Per cent set after being stretched—				
		100	200	300	400	500
1	Repeated stretch	1.0	4.5	9.5	16.0	25.0
	Single stretch	....	....	11.7	19.8	29.0
2	Repeated stretch	1.8	4.0	7.7	13.7	21.2
	Single stretch	....	....	8.0	14.7	21.5
3	Repeated stretch	3.7	9.0	17.7	27.0	37.0
	Single stretch	....	....	21.7	34.0	47.0
4	Repeated stretch	4.0	12.3	28.7	48.7	....
	Single stretch	....	14.3	33.0	56.0	....
5	Repeated stretch	8.1	19.4	34.0	....	....
	Single stretch	....	19.3	33.0	....	....
6	Repeated stretch	4.3	16.3	34.0	....	....
	Single stretch	....	17.0	35.3	....	....

It will be noted that the effect of previous stretching is very marked in the case of Nos. 1, 3, and 4; that it is very slight in the case of Nos. 2 and 6; and that in the case of No. 5 the set is slightly increased by previous stretching.

(7) *Influence of the Form of Test Piece on the Results of Tension Tests.*—There is a wide difference of opinion in regard to the relative merits of the straight and ring-shaped test pieces. The ring,

which is highly recommended by some, undoubtedly possesses certain advantages as regards convenience in testing, and uniform results may be obtained by this method.

Ring test pieces, however, do not show the full tensile strength of rubber, on account of the uneven distribution of stress over the cross section. This fact is evident from a simple analysis, and may be verified by comparative tests with straight and ring-shaped test pieces, provided the straight test pieces are sufficiently enlarged at the ends to prevent failure in the grips, and provided further that the change in width is not made too abruptly.



AFTER STRETCHING

BEFORE STRETCHING

Fig. 20.—*Ring test piece before and after being stretched*

Assuming for simplicity that the extensibility of rubber is the same in all directions, it will be seen by reference to Fig. 20, which represents a ring test piece before and after extension, that,

If E_1 = per cent elongation of the inside surface at breaking point (automatically measured),

then $E_1=\frac{L_1-l_1}{l_1}.100$ . . . . (1)

If E_2 = per cent elongation of the outside surface when specimen breaks,

$$\text{then } E_2 = \frac{L_2 - l_2}{l_2} . 100 \qquad (2)$$

$$L_2 = L_1 + \pi/2\ (D_2 - D_1) = L_1 + \pi T \qquad (3)$$

$$T = t\sqrt{\frac{l_1}{L_1}} \text{ approximately} \qquad (4)$$

(assuming that the volume of rubber is constant.)

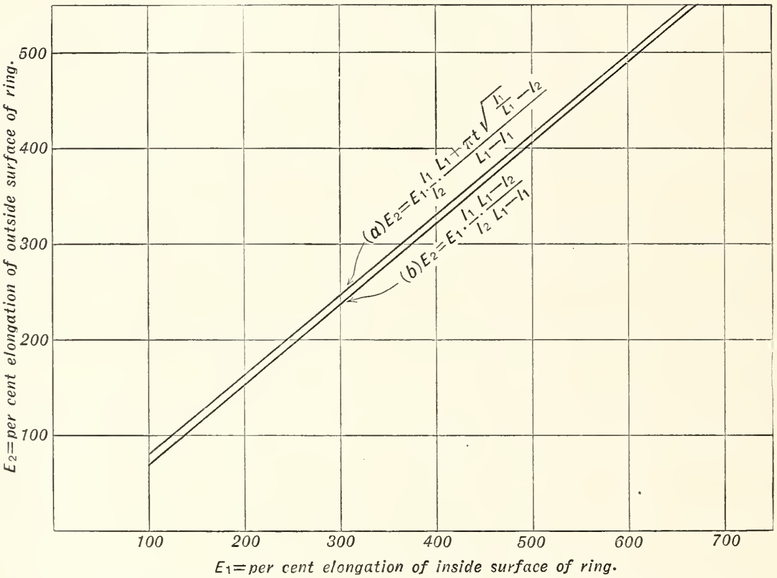


FIG. 21.—*Relation between the elongation at the inside and outside of a ring*

From equations 1, 2, 3, and 4 we have

$$E_2 = E_1 \cdot \frac{l_1}{l_2} \cdot \frac{L_1 + \pi t\sqrt{\frac{l_1}{L_1}} - l_2}{L_1 - l_1} \qquad (5)$$

which is represented graphically in Fig. 21 (*a*) for the usual size of ring in which $l_1 = 70$ mm and $t = 4$ mm.

This relation is practically a linear one, and $E_2 = 0.83E_1$ approximately. Fig. 21 (*b*) shows the slight error introduced by neglecting the term $\pi t\sqrt{\frac{l_1}{L_1}}$

Now, since the percentage of elongation at the outside surface of the ring is less than at the inside surface, the tensile stress must also be less at the outside than at the inside surface. From equation (5) it follows that the decrease in the per cent of elongation is approximately uniform from the inside to the outside of the ring, this relation being shown in Fig. 22 for $E_1 = 600$ per cent and $l_1 = 70$ mm. The relation between stress and elongation being practically a linear one for values of elongation near the breaking

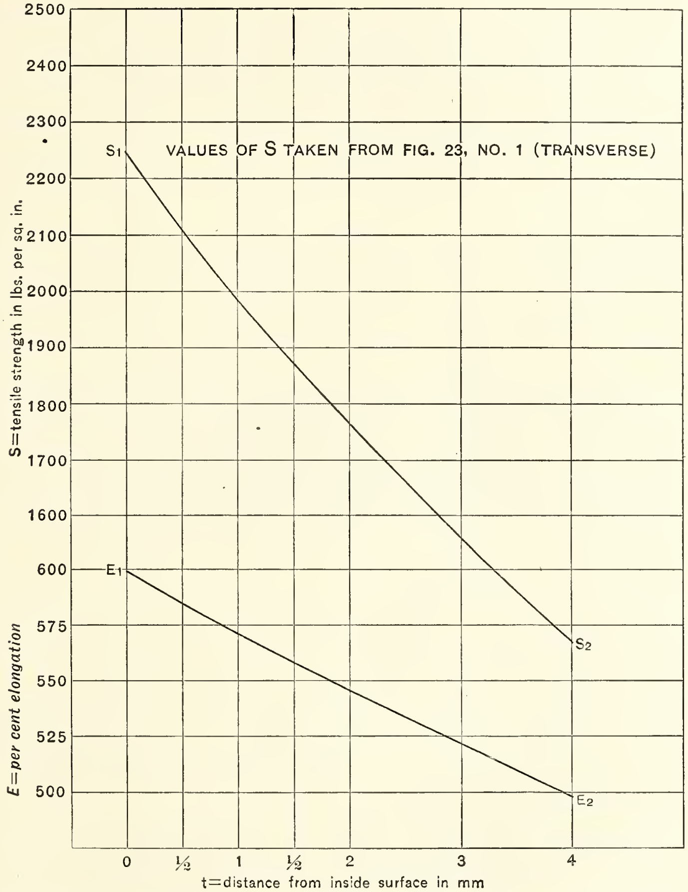


FIG. 22.—*Variation in elongation and tensile strength from the inside to the outside of a ring*

point, the decrease in tensile stress must also be fairly uniform from the inside to the outside of the ring at the time of failure. This is illustrated graphically in Fig. 22, in which the values for tensile stress were taken from the stress-strain diagram shown in Fig. 23, No. 1.

If S_1 = the stress at the inside surface of the ring at failure, or true tensile strength of the rubber corresponding to E_1, and S_2 = the stress at the outside surface, corresponding to E_2, and S = the average stress over the cross section of the ring, which is the value for tensile strength obtained by the ring method, we have

$$S=\frac{\text{Breaking load}}{\text{Area of section}}=\frac{S_1+S_2}{2}=\frac{S_1}{2}\left(1+\frac{S_2}{S_1}\right)\text{ approximately} \ldots\ldots (6)$$

Now, since the ratio $\frac{S_2}{S_1}$ varies for different rubbers, S does not bear a constant ratio to, and, therefore, can not be taken as a measure of tensile strength. Elongation, however, is measured at the inside surface of the ring and, therefore, represents the maximum extension of the rubber around the inside of the ring. The average elongation over the cross section of the ring is,

$$E=1/2\ (E_1+E_2)\text{ approximately} \ldots\ldots (7)$$

If the extensibility of rubber were the same in all directions, values of S and E obtained from equations (6) and (7) would, theoretically, give a point lying very near the stress-strain curve for the same rubber tested in the form of a straight specimen. This, however, is not the case, as has been already pointed out, and as may be seen from Fig. 23.

The difference between S and S_1 is greater for high-grade rubbers than for compounds of poor quality, as may be seen by reference to Fig. 23, which represents stress-strain curves plotted from the results of tests on straight and ring specimens. Table 8 shows values for tensile strength and ultimate elongation obtained for the same rubbers by the two methods.

The ring test piece obviously does not give a true stress-strain curve on account of the varying stress over its cross section.

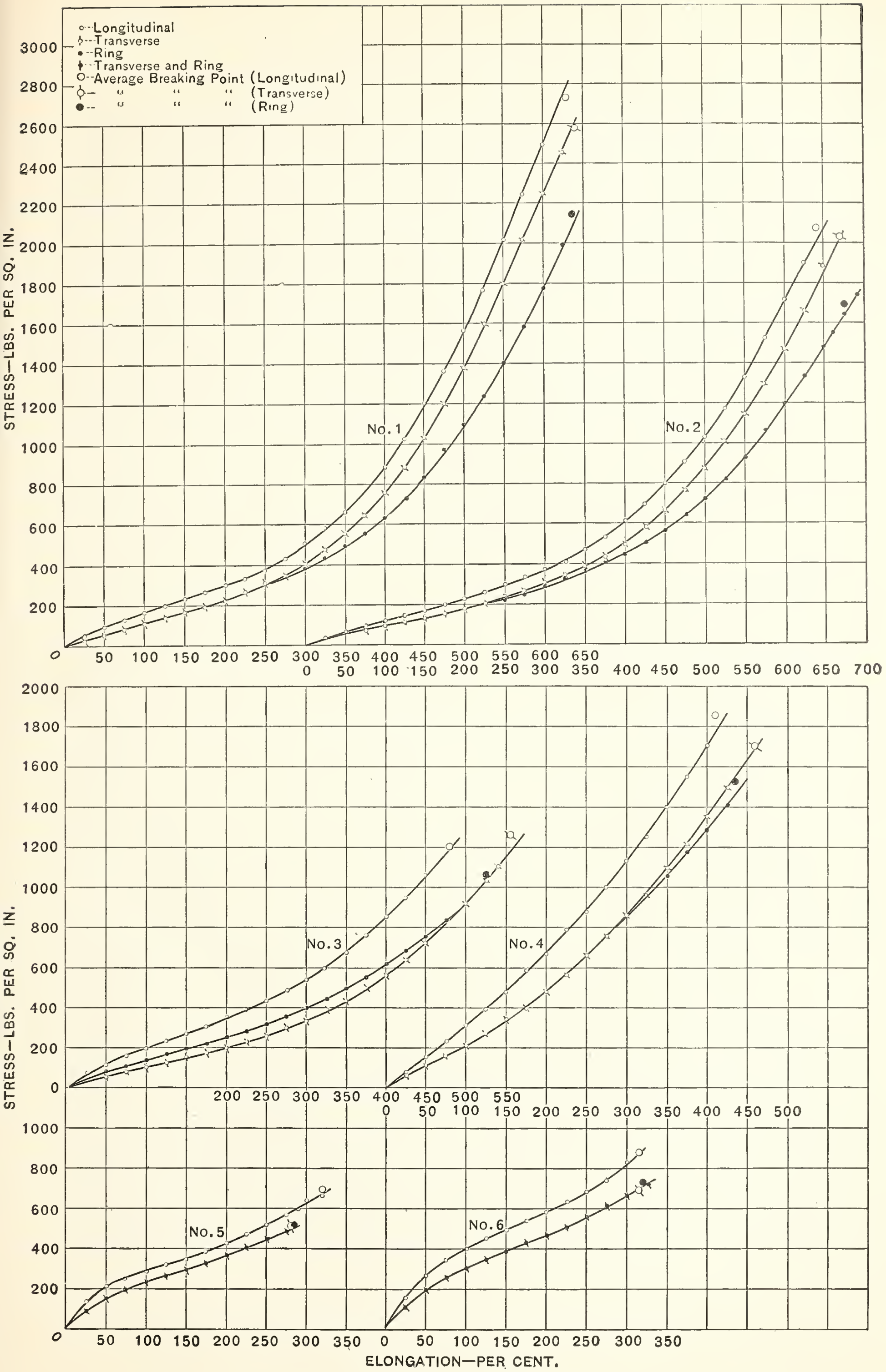


Fig. 23.—*Stress-strain curves for rubber tested with straight and ring-shaped specimens*

Straight specimens were cut both longitudinally and transversely, with reference to the direction in which the rubber had been passed through the calender rolls. They were tested with the machine shown in Fig. 11, and the ring specimens were tested with a Schopper machine, Fig. 15. In each case the specimens were stretched at the rate of about 8 inches per minute. A number of test pieces, both straight and ring shaped, particularly in the case of No. 3, showed abnormally low tensile strength and elongation on account of small holes or particles of grit at the point of rupture. Such specimens are not included in the results tabulated below, each of which represents the average of from 5 to 15 tests.

TABLE 8

Results Showing the Relative Strength and Elongation of Rubber Tested with Straight and Ring Shaped Specimens

Rubber compound No.	1	2	3	4	5	6
Tensile strength (pounds per square inch):						
Straight specimens—						
Longitudinal (L) [5]	2730	2070	1200	1850	690	880
Transverse (T)	2575	2030	1260	1700	510	690
Ring specimens (R)	2140	1690	1060	1520	510	730
R/L	0.78	0.82	0.88	0.82	0.74	0.83
R/T	0.83	0.83	0.84	0.89	1.00	1.06
Ultimate elongation (per cent):						
Straight specimens—						
Longitudinal	630	640	480	410	320	315
Transverse	640	670	555	460	280	315
Ring specimens	635	675	525	435	285	320

[5] Longitudinal—indicates the direction in which the rubber has been passed through the calender rolls.

A line was drawn across each of the ring specimens to indicate the longitudinal direction, and the point of failure was noted. There was a tendency for the rings to rupture along this line, thus indicating that the sheets were strongest longitudinally, or in the direction of rolling. This difference in strength is shown by the straight test pieces, except in the case of compound No. 3. It is seen from Fig. 23 that the curve for transverse specimens lies below that for longitudinal specimens, thus showing that a given stress will produce a greater elongation if applied transversely than if applied longitudinally. It is to be expected, therefore, that the elongation of a ring will be less than that for a transverse straight specimen. The natural variation in rubber, however, is often sufficient to obscure small differences in elongation due to the methods of testing.

In the case of Nos. 5 and 6, the curves for the ring specimens practically coincide with those for the transverse straight specimens, and the tensile strength of these rubbers when tested by the two methods is seen to agree fairly well. It is to be noted, however, that for the higher-grade rubbers the difference in tensile strength by the two methods is very marked. Although the difference is not great, there is a tendency for the transverse specimens to show a greater ultimate elongation than the longitudinal specimens, notwithstanding the greater strength shown in the latter case.

(*e*) "FRICTION" TEST.—The "friction" or adhesion between the plies of canvas on rubber hose and between the canvas and the rubber tube and cover is of great importance—in fact, the life of hose depends in great measure upon the efficiency of this adhesion. The same is true and to an even greater extent in the case of rubber belting.

The friction of "plied" hose is determined in the following manner (Fig. 24): In preparing test pieces, a short length of hose is pressed tightly over a slightly tapered mandrel, such as the ones shown. The mandrel is put in a lathe, and 1-inch rings are cut with a pointed knife. Beginning at the lap a short length of canvas is separated, and the ring is pressed snugly over a mandrel, which is free to revolve in roller bearings. The rate at which the canvas strips under the action of a specified weight suspended from its detached end is taken as a measure of the friction.

A marked difference is often found in the friction between different plies of the same hose, as well as at different points along the same ply. Uniformity in the friction is desirable.

The results of this test are influenced by the temperature conditions, the rate of stripping caused by a given weight being greater at high than at low temperatures. Also, the rate of stripping is greater if the mandrel fits snugly in the ring than if the ring is allowed to sag over a loose mandrel. The variation in friction, however, in the same hose is often such as to obscure these influences, unless observations are made under conditions which differ greatly.

In connection with this test, attention may be called to a point which, though generally recognized, is sometimes lost sight of in the interpretation of results.

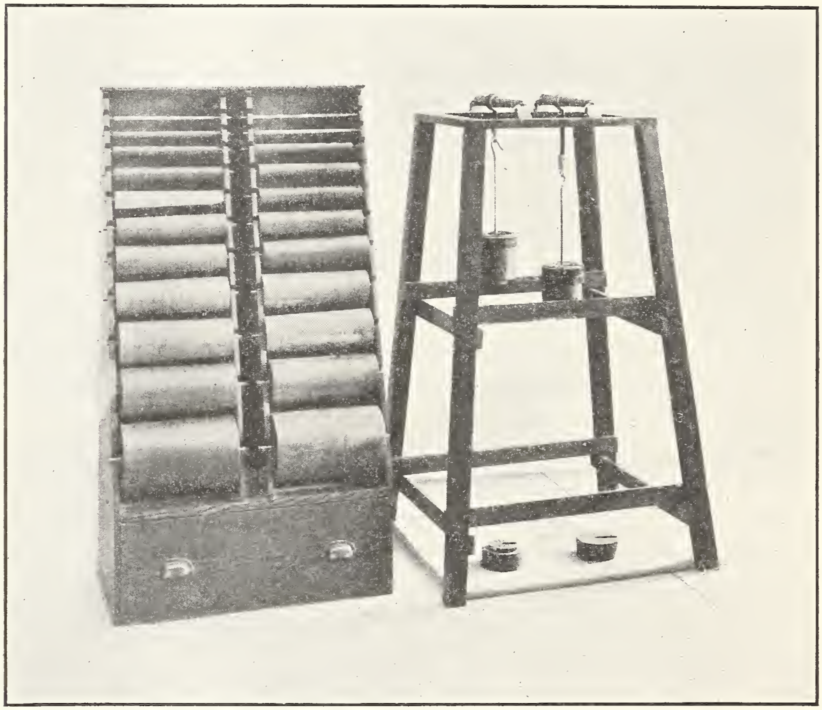


FIG. 24.—*Apparatus for testing the "friction" of rubber hose*

It has been observed that no stripping is produced by increasing the weight up to a certain point, after which the rate of stripping increases gradually at first, and then more rapidly, with small increments in weight, until finally a very small increase in weight causes a large change in the rate of stripping. The general behavior is illustrated graphically in Fig. 25, in which each point represents the average of a number of tests on a very uniformly frictioned hose.

As a result of this behavior, an air hose, for example, which is required to show a rate of stripping not exceeding 6 inches in 10 minutes under 25 pounds, might be regarded as of very inferior quality if it stripped, say, 20 inches in 10 minutes, whereas the same hose would probably show little or no stripping under 20 pounds and come within the required limit under 22 pounds.

The "friction" of rubber-lined fire hose is usually tested as follows: A 1½ or 2 inch strip is cut transversely from the hose (the sides being parallel to the filler strands). The strip thus prepared is laid out flat and the rubber lining cut through to the jacket along parallel lines 1 or 1½ inches apart, as may be desired.

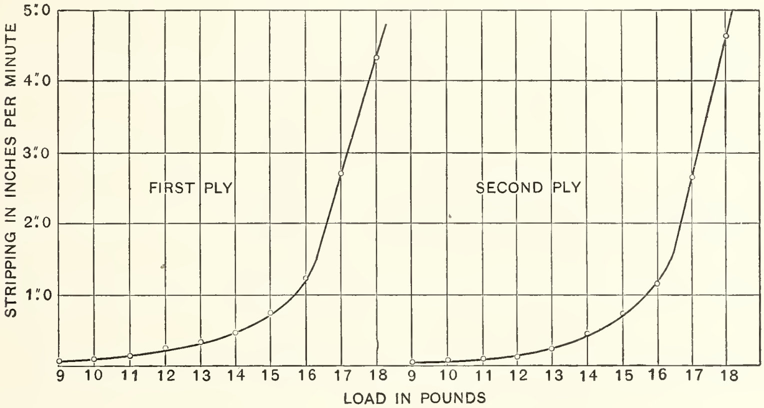


FIG. 25.—*"Friction" test of rubber hose. Curves showing rate of stripping under different loads*

The central portion of the lining is separated from the jacket for a short distance. The detached end of the jacket is clamped in a stationary grip, and the weight is suspended from the rubber lining.

The "friction" between the plies of duck in rubber belting is sometimes tested by applying the load in a direction at right angles to the plane of separation, as in the case of "plied" hose. As shown in Fig. 26, A, this is done by cutting the belt about halfway through along parallel lines 1 inch apart. The belt rests on horizontal supports just outside of the strip which has been cut, and the weight is suspended from the detached end of the duck.

A more usual method is that shown in Fig. 26, B, where a 1-inch strip is held in a fixed clamp with the weight suspended from the end of a detached layer of duck. In testing by this method it will be found that the angle of separation varies somewhat according to the thickness of the strip and that the results are thereby influenced to some extent. The difficulty may be avoided by subdividing the 1-inch section into strips of two plies each, as shown in Fig. 26, C, and very satisfactory results are obtained in this way. It is found that for a given weight the rate of stripping is decidedly greater by methods B and C than by method A. Fig. 27 shows graphically the results obtained by the three methods.

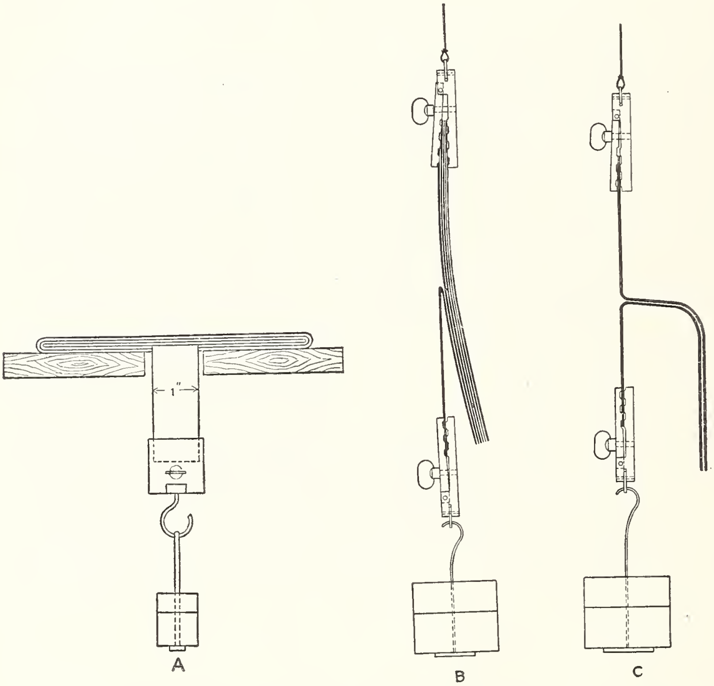


FIG. 26.—*Illustrating methods of testing the "friction" of rubber belting*

(*f*) HYDRAULIC-PRESSURE TEST.—The pressure test as usually made consists simply in subjecting a short length of the hose to water pressure created by a force pump of any convenient type.

The coupling at the free end is closed with a plug, and the pump connection is made with a reducing coupling. By using two clamps at each end it is possible to make a tight joint even under high pressure. It is necessary to provide a check valve to protect the pressure gauge against shock when a hose bursts. A pet cock should be provided to release the air as the hose is being filled.

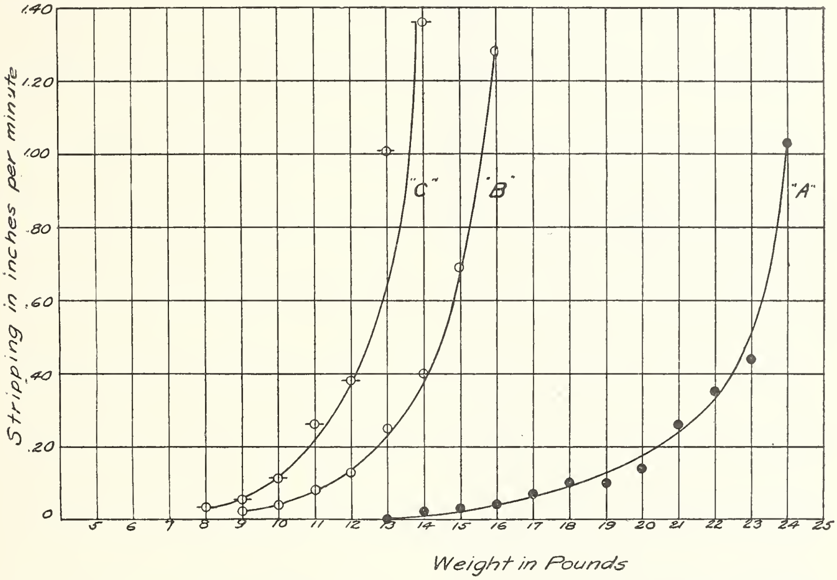


FIG. 27.—"*Friction*" *test of rubber belting. Curves showing rate of stripping when tested by methods illustrated in Fig. 26*

Requirements of specifications as regards the pressure test vary according to the kinds of hose, but, as a rule, the test is made not with the view of developing the ultimate strength of the hose but rather to detect defects in workmanship, which are usually noticeable at a pressure well below that necessary to rupture the hose.

In the case of fire hose it is usual to specify a certain pressure when the hose is lying straight or when bent to the arc of a circle of given radius, and the hose must stand a specified pressure when doubled upon itself. It must not show excessive expansion, elongation, warping, or twist under pressure, and the twist must be in a direction tending to tighten the couplings.

(*g*) STEAMING TEST.—Fig. 28 illustrates a method of testing steam hose. The header 1 is provided with six outlets, each of which is controlled by a ½-inch globe valve. The header 2, which is connected to a steam trap 3, is similarly provided with inlets and controlling valves. The hose to be tested is cut into lengths that will just fit between the connections on the headers, the bottom connections being made with unions. Steam passes through a regulating valve (not shown) into the header 1 and thence through the hose to the header 2, from which the condensation is carried to the steam trap.

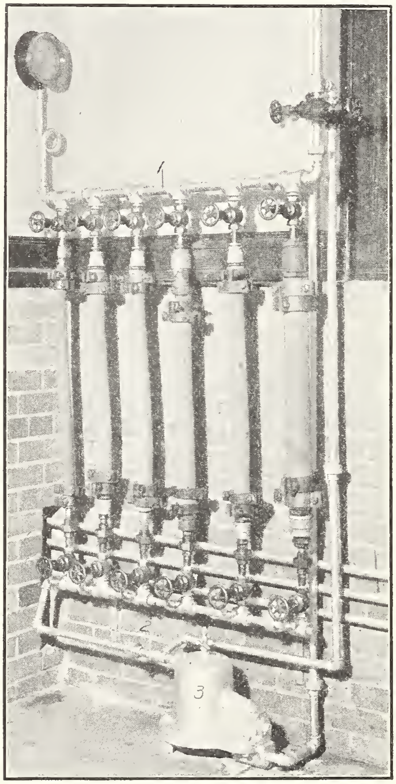


FIG. 28.—*Six samples of steam hose connected up for steaming test*

(*h*) TESTING THE RUBBER INSULATION OF WIRE.—The mechanical tests that are usually specified for the rubber insulation of wire are the same as those already described in connection with tension tests.

The method of preparing test pieces, however, is not always the same, but depends upon the size of conductor and the character of insulation.

If the wire is of small diameter, it is desirable to remove the insulation as a whole, in which case the test piece is in the form of a tube. To do this, if the adhesion of the rubber to the wire is not great, it is sometimes possible, by careful manipulation of the insulation, to work it off of the wire. The end of the wire which is drawn through the insulation should be carefully rounded to prevent injury to the rubber. If the adhesion between rubber and wire is so great as to make it difficult or impossible to remove the wire in this way, the wire may be stretched beyond its elastic limit in a testing machine, and by thus reducing its cross section it is usually a simple matter to remove the insulation. Sometimes even this stretching of the wire fails to permit of the rubber being easily removed. In this case the insulation is cut longitudinally with a sharp knife held perpendicular to the wire, after which the wire may usually be removed without difficulty.

In the case of large conductors test pieces are sometimes prepared by cutting a strip of the insulation with a knife held tangent to the wire. A sharp knife should be used, and the blade should be wetted before each cut.

If the conductor is of sufficient size and if the thickness of the insulation is small in proportion to its diameter, test pieces may be obtained as follows: The insulation is cut in a longitudinal direction and the wire removed. Then, with the die shown in Fig. 7, test pieces with enlarged ends are cut. The operation of cutting with the die is facilitated by spreading the insulation out flat and holding it down with pins.

When practicable, this form of test piece should be used, for the reason that with specimens of uniform cross section over their entire length it is often impossible to prevent the rubber from tearing in the grips. In the case of a stranded conductor the inside surface of the insulation retains the impression of the wires. To secure a satisfactory test piece whose cross section may be accurately measured, the surface should be ground smooth with an emery wheel. (See Fig. 6.)

A type of grip commonly employed for testing rubber insulation when test pieces of uniform cross section are used is illustrated in Fig. 10, *c*, but it has been found that in most cases the grip shown in Fig. 10, *A*, gives equally satisfactory results. The latter grip has the advantage of requiring a much shorter test piece, and it is easier to operate.

(*i*) COMPARATIVE TESTS OF MACHINE AND HANDMADE TUBES.—A question is sometimes raised as to whether the tube of a hose has been made in a tubing machine or from calendered sheet. Calendered tubes are often specified, and since it is sometimes impossible to determine by inspection if a tube is machine-made or handmade, a test that could be depended upon in all cases to distinguish between the two kinds of tubes would serve a useful purpose.

From the nature of the case a chemical analysis could not determine this point, because a compound might be calendered or run through a tubing machine without in any way altering its composition. The mechanical properties of a compound, however, are influenced to a greater or less extent by the method of manufacture.

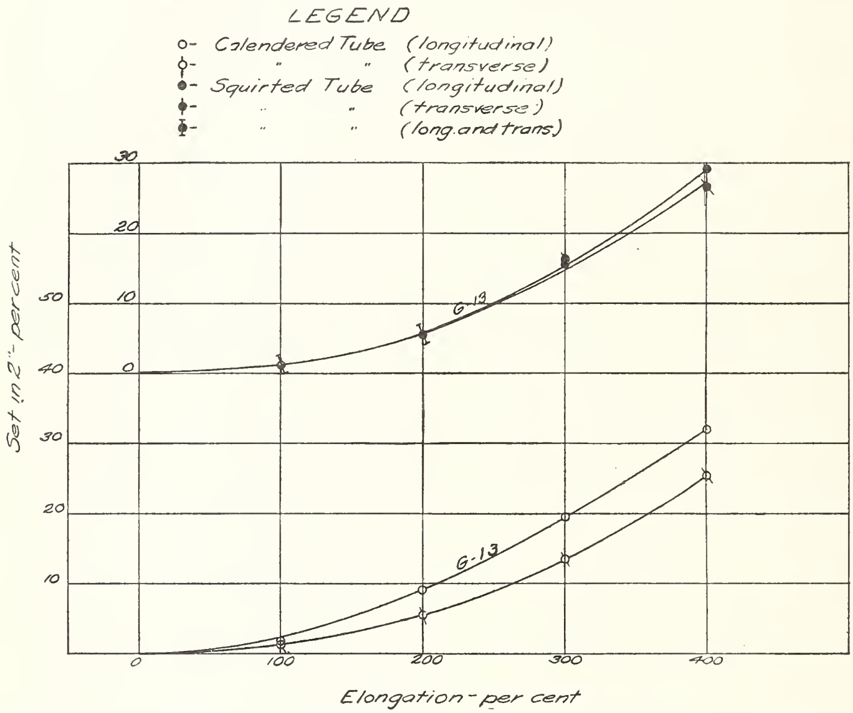


Fig. 29.—*Curves showing the comparative elasticity of a "squirted" and calendered tube, tested in the longitudinal and transverse directions*

Comparative results for elasticity or "set," tensile strength, and ultimate elongation are given in Table 9. Each of the three compounds was made into two tubes of the same size, one from calendered sheet and the other made in a tubing machine. The conditions of vulcanization were the same for each pair of tubes, so that any difference in their physical properties is fairly attributable to the effects of the tubing machine and calender rolls.

In comparing the results it is interesting to note that the squirted tubes show practically the same set when tested longitudinally and transversely, whereas the calendered stocks are much more elastic in the transverse direction, as has been pointed out in connection with tests previously described. This is more clearly illustrated in Fig. 29 which shows graphically the relation between set and elongation for test pieces cut longitudinally and transversely from the compound G–13. In the same way Fig. 30

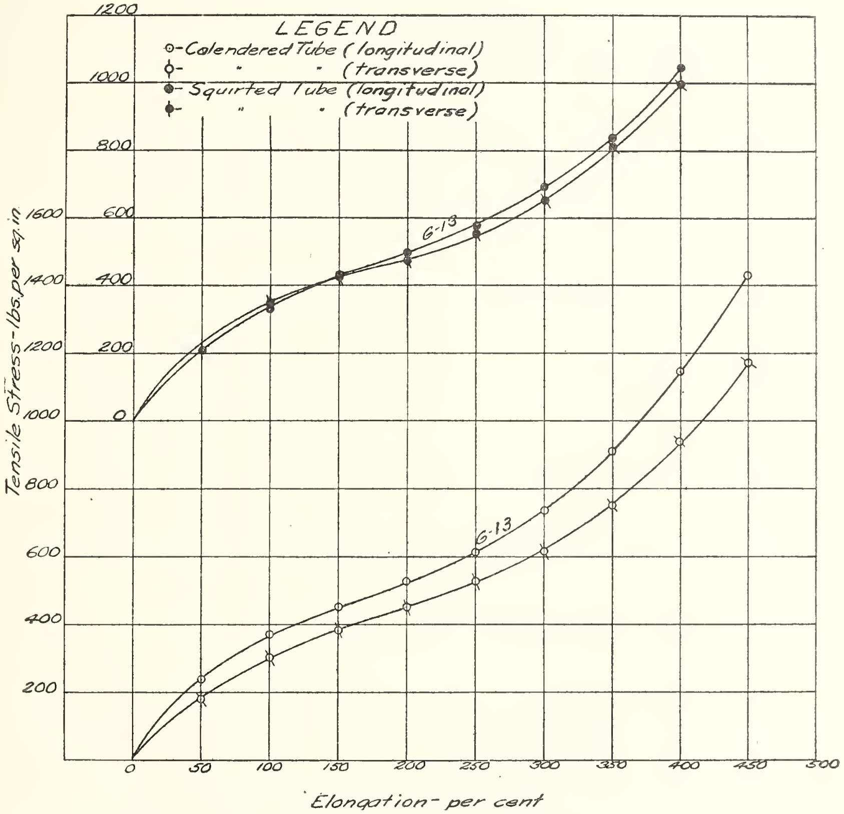


FIG. 30.—*Stress-strain curves for a "squirted" and calendered tube, tested in the longitudinal and transverse directions*

shows stress-strain curves for G–13. Similar tests of the other two compounds could not be made for lack of material.

Definite conclusions should not be drawn from these preliminary tests, but the results, which indicate that the elastic properties of squirted stock are practically the same in all directions for extensions up to at least 75 per cent of the ultimate elongation, may be verified by further experiments which will be made the subject of a separate paper.

TABLE 9

Relative Strength, Elongation, and "Recovery" of "Squirted" and Calendered Tubes when Tested in the Longitudinal and Transverse Directions

Rubber No.	V–14		V–16		G–13	
Kind of tube	Calendered	Squirted	Calendered	Squirted	Calendered	Squirted
Set[6] after 1 minute stretch and 1 minute rest (per cent):						
Longitudinal	11.7	12.5	24.7	23.0	26.0	22.5
Transverse	10.5	12.5	20.0	21.8	18.5	21.5
Tensile strength (pounds per square inch):						
Longitudinal	520	460	1450	1310	1110	1130
Transverse	530	460	1380	1290	1295	1330
Ultimate elongation (per cent):						
Longitudinal	275	240	530	525	455	470
Transverse	290	235	535	505	510	510

[6] V–14 was stretched 200 per cent; V–16 and G–13, 350 per cent.

2. BUREAU OF STANDARDS PROCEDURE FOR PHYSICAL TESTING OF RUBBER

Unless otherwise specified the following method of procedure will be followed in testing rubber at the Bureau of Standards:

Temperature.—All tests will be made at 75° F.

Test Pieces.—Test pieces used for the determination of "set," tensile strength, and ultimate elongation will be one-fourth inch wide with 2-inch gauge length (Fig. 8), except when the ultimate elongation is greater than 700 per cent, in which case the gauge length will be 1 inch. In the case of hose, test pieces will be cut longitudinally. All impressions of the fabric will be removed with the emery wheel shown in Fig. 6. The same test pieces will be used in determining "set" and tensile strength.

Thickness.—Thickness will be measured with the spring micrometer shown in Fig. *9B*.

"*Set.*"—Set will be determined as described on page 34, III–1–(*b*), and test pieces will be stretched to the specified elongation in from 10 to 15 seconds, which time will be included in the stretch period. The period of rest will be measured from the instant the test piece is released.

Tensile Strength and Ultimate Elongation.—Tensile strength and ultimate elongation will be determined as described on pages 20–34, III–1–(*a*). The grips will be separated at the rate of 20 inches per minute.

Friction.—In testing plied hose, friction will be determined as described on page 49, III–1–(*e*), using a 1-inch ring pressed snugly over a slightly tapered mandrel.

Cotton rubber-lined hose will be tested as described on page 51, III–1–(*e*), the test piece being cut in the transverse direction and the load applied to a strip 1 inch wide.

Rubber belting will be tested as described on page 52, III–1–(*e*) (Fig. 26, C), using a strip 1 inch wide.

IV. THE CHEMISTRY OF RUBBER

1. GENERAL DISCUSSION

Although rubber has been extensively used for a number of years, it is only recently that we have had any clear conception of its chemical nature. The synthesis of rubber from isoprene, a terpene having the formula C_5H_8, shows that it is probably a polyterpene having the formula $(C_{10}H_{16})x$. The exact size of the molecule is still unknown. The correctness of the above formula is further demonstrated by Harries and others in their work on the various addition products, such as the tetrabromide, nitrosite, ozonide, etc.

Rubber is one of a class known to chemists as unsaturated compounds—that is, they possess the power of reacting with certain substances by direct addition. The addition products mentioned above are the result of such reactions. Rubber is capable in like manner of uniting with sulphur, particularly at the elevated temperatures, such as are used in the process of vulcanization. Each group of $C_{10}H_{16}$ can combine with two atoms of sulphur. It is this addition of sulphur during the process of vulcanization which transforms the crude gum into the more serviceable commercial material. The addition of sulphur is not necessarily carried to the point of saturation. If only a small amount is added, as in the so-called soft-cured articles, products are obtained which are tough and elastic, while with increasing sulphur content the rubber becomes harder, until with the maximum amount of sulphur which will combine with the rubber the material known commercially as hard rubber, ebonite, vulcanite, etc., is obtained.

The crude rubbers, however, contain other substances than the pure rubber above mentioned. In addition to scraps of bark, twigs, dirt, etc., that accompany some of the crude rubbers, they contain varying proportions of proteids, resins, hydrocarbons, etc. In some cases the rubber is only a very small fraction of the entire mass, and then it requires extensive treatment to obtain the pure gum. The mechanical impurities and water-soluble constituents are removed by the washing process described elsewhere in this circular. The resins remain behind and form one impurity which must be determined by chemical analysis. The amount and character of these resins are of great assistance in determining the nature of the rubber used in compounding. The percentage of resins in some crude rubbers is exceptionally high, and the latter must be subjected to a deresinizing process before they can be used.

To give a complete discussion of the chemistry of rubber would require more space than the scope of this circular would permit. However, such a discussion is not necessary, since the chemistry of rubber is not involved to any great extent in the chemical analysis of rubber goods. In addition to the rubber and sulphur, rubber goods may contain fillers, such as litharge, whiting, zinc oxide, barytes, sublimed white lead (a basic sulphate of lead containing some zinc oxide), etc.; reclaimed rubber and rubber substitutes; vaseline; ceresin or paraffin, etc. The analysis of rubber goods includes not only the determination of the percentages of rubber and sulphur, but also of the acetone-soluble oils, waxes, resins, and rubber substitutes which may be present.

2. EXPLANATION OF THE ANALYSIS

It frequently happens that people who are not familiar with the manufacture of rubber goods and who know little of the chemistry involved are called upon to interpret the chemical analysis of such material. In order that such people may understand the reasons for making certain determinations and their significance, a brief explanation of some of the more important steps in the procedure is given below.

(*a*) Acetone Extract.—If the acetone extraction is made on, a vulcanized compound, the acetone extracts the rubber resins the free sulphur, and any mineral oils or waxes that may have been used. The percentage of free sulphur is determined and deducted from the total extract. The corrected figure thus obtained will at times give valuable information regarding the quality of the rubber present. For the best grades of Para rubber this should not exceed 5 per cent of the rubber present. A higher extract would indicate the presence of other rubbers than Para, while the presence of mineral oil would indicate the possibility of reclaimed rubber having been used, inasmuch as practically all the reclaimed rubbers are compounded with more or less mineral oil (usually vaseline) to make them work more easily.

The acetone extraction is one of the most promising and useful tests for the examination of rubber goods. A vast amount of work remains to be done before the analyst will always be in a position to say exactly what has been used in compounding. Even to-day, however, a great deal of information can be obtained from it.

(*b*) Free Sulphur.—The free sulphur is that part of the sulphur originally added as such which remains unchanged after vulcanization. Small amounts of free sulphur are not harmful, but there are some who object to it in excessive amounts, claiming that in such cases it increases the rate of deterioration of the rubber. It is difficult, however, to place a limit beyond which the free sulphur is to be considered excessive.

A limit is usually placed on the free sulphur in high-grade insulation compounds, not particularly on account of its effect on the rubber, but because it may corrode the copper wire.

(*c*) TOTAL SULPHUR.—Sulphur occurs in vulcanized rubber as free sulphur, in combination with the rubber, and at times in the mineral fillers, reclaimed rubber, and rubber substitutes.

It is limited by specification in high-grade material, in order to eliminate undesirable sulphur minerals and prevent as far as possible the use of inferior or reclaimed rubbers and rubber substitutes. The inferior rubbers require a larger percentage of sulphur than Para for proper vulcanization, while the reclaimed rubber and substitutes contain usually large amounts of sulphur. If it is desired to have material made from Para rubber only, the effect of placing the limit for sulphur where it will just suffice for the vulcanization of the amount of Para required will be to make it difficult to use these inferior grades and still have the total sulphur fall within the specified limit.

(*d*) ASH AND SULPHUR IN THE ASH.—The ash is the residue left after ignition, consisting principally of the nonvolatile mineral fillers. The percentage of ash is of no great importance in itself but is used in the calculation of the rubber present, as will be explained later.

The sulphur in the ash consists of the sulphur from some of the mineral fillers, and also part of the sulphur that was combined with the rubber, but which during ignition enters into combination with one or another of the mineral fillers. Its amount is determined merely for the purpose of obtaining a correction figure and has no other significance.

(*e*) BARYTES.—It has been stated above and elsewhere that sulphur may be present in the mineral fillers. There can be no objection to such sulphur, provided the mineral containing it has no injurious effect on the rubber, and further that the amount of such sulphur can be readily determined. Barytes is such a substance, and it is permitted in practically all compounds where the amount of sulphur is limited by specifications. There are no other fillers which as yet fulfill both of the conditions named.

(*f*) RUBBER.—The determination of the amount of rubber present in a vulcanized compound is an important though difficult matter. For a long time this was determined by igniting a weighed sample and determining the mineral fillers or ash. The rubber was calculated by the difference between 100 per cent and the sum of the ash (sulphur-free), total sulphur, and corrected acetone extract. This procedure is still extensively used, and although it can not be depended upon always to give accurate results, it is probably as good as any method yet devised.

The problem is to-day being attacked from several points. Some chemists are endeavoring to find a suitable solvent which will remove the rubber and permit the weighing of the mineral residue. Turpentine, terebene, anisole, phenetole, and many others have been suggested, but even the best of them give only fair results. Other chemists are working along the line of the direct determination of the rubber present by means of the various addition products, such as tetrabromide, nitrosite, etc., and the results obtained are still far from satisfactory.

(*g*) SPECIFIC GRAVITY.—The specific gravity of the various constituents of vulcanized rubber differs greatly. The percentages are, however, always expressed by weight. It is apparent, therefore, that with equal percentages by weight, a compound of specific gravity of, say, 1.5 will have less rubber per unit volume than one of a higher specific gravity. In order to insure a minimum volume of rubber, specific gravity limits are stated.

(*h*) WAXY HYDROCARBONS.—The efficiency of rubber as an insulator is very much lessened by the absorption of moisture. To prevent this, small amounts of paraffin or ceresin are added. Their presence is usually permitted in specifications, the limit being generally placed at 4 per cent, although the tests made in this Bureau would indicate that the maximum amount is seldom necessary. The amount of such waxy hydrocarbons is determined not only in order to learn if the specifications have been complied with, but also to obtain the percentage of acetone extract from the rubber itself.

(*i*) CHLOROFORM EXTRACT.—The so-called mineral rubbers such as tar, bituminous substances, elaterite, gilsonite, etc., are used extensively as rubber substitutes. These substances are partly soluble in acetone, but the material so removed is not characteristic of these substitutes and is not readily distinguished from vaseline and similar mineral oils. Part of the insoluble portion remaining after the treatment with acetone is soluble in chloroform, the solution being very dark in color. Properly vulcanized high-grade rubbers yield only a small amount during the chloroform extraction, the solution being practically colorless.

(*j*) ALCOHOLIC-POTASH EXTRACT.—Some of the rubber substitutes are prepared by the action of sulphur or sulphur chloride on vegetable oils. The purpose of the alcoholic-potash extraction is to detect the presence of such substitutes and to give some idea of the amount. Para rubber contains only a small percentage of material extracted by this solvent.

3. BUREAU OF STANDARDS METHODS OF ANALYSIS

The methods given below are essentially as they appear in the sheets of instructions handed to all rubber analysts in the Bureau. They are not entirely original, but have been compiled from the various publications on rubber analysis, from the information gained through the routine testing of rubber goods for delivery on Government contracts, and from cooperative research with various scientific organizations. These methods are subject to revision whenever the Bureau is convinced that changes would improve them.

(*a*) PREPARATION OF SAMPLES.—

(1) *Soft Rubber.*—A sample of not less than 25 grams shall be prepared by taking pieces from various parts of the original sample. With those having cover and tube, separate samples of each shall be made. From fire hose remove the backing before grinding.

(2) *Grinding.*—The sample shall be cut into small pieces and then run through a grinder, taking for analysis only such material as will pass a 20-mesh sieve. Care must be taken to see that the grinder does not become appreciably warm during the grinding. If the nature of the material is such that it gums together so that it will not pass through the sieve (as would be the case with undervulcanized samples), it will be sufficient to pass the material through the grinder twice and accept all the material for the final sample. Crude rubber shall be cut with scissors.

(3) *Hard Rubber.*—Samples of this material shall be prepared for analysis by rasping.

(*b*) REAGENTS.—

(4) All reagents shall be of C. P. quality, specially tested before use.

(5) Acetone shall be freshly distilled over anhydrous potassium carbonate, using the fraction obtained at 56° to 57° C.

(6) Alcoholic potash shall be of normal strength, made by dissolving the required amount of potassium hydroxide in absolute alcohol and allowing it to settle. Only the clear solution shall be used.

(7) The nitric acid-bromine reagent shall be prepared by adding a considerable excess of bromine to concentrated nitric acid, shaking thoroughly, and allowing it to stand for some hours before using.

(8) The fusion mixture for sulphur determinations shall be made by mixing equal quantities of sodium carbonate and powdered potassium nitrate.

(9) Barium-chloride solution shall be made by dissolving 100 grams of barium chloride in 1 liter of distilled water and adding 2 or 3 drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness, the solution shall be heated on the steam bath overnight and filtered through 589 S. & S. blue-ribbon filter paper.

(*c*) ANALYSIS OF MECHANICAL GOODS.—

(10) *Acetone Extract.*—Place a 2-gram sample in an acetone-extracted S. & S. paper thimble, and extract continuously with acetone for eight hours (see Fig. 31), unless the solution in the thimble is still colored at the end of that time, when the extraction shall proceed the next day for a further period of four hours. Transfer the extract to a tared 100 or 150 cc Erlenmeyer flask, using chloroform or benzene for dissolving any material which may have separated from the solvent during the course of the extraction. Drive off the solvents at as low a temperature as possible, using a gentle current of air. Dry the flask and contents in an air bath at 90° to 95° C; cool and weigh. Call the residue "acetone extract, uncorrected." Calculate the results to percentage.

(11) *Free Sulphur.*—Add to the flask (paragraph 10) containing the acetone extract uncorrected 50 to 60 cc of distilled water and 2 or 3 cc of bromine. (If the acetone extract indicated a large amount of free sulphur, the amount of bromine used may be increased.) Heat gently on the steam bath until the solution is practically colorless, and filter into a 250-cc beaker. Cover the beaker with a watch glass, heat to boiling on the steam bath, add 10 cc of 10 per cent barium chloride solution, and allow the precipitate to stand overnight. The next day filter the precipitate on a 11-cm 590 S. & S. filter paper. Ignite in a small porcelain crucible, using a small Bunsen flame and not allowing the paper to inflame; cool and weigh. Calculate the barium sulphate to sulphur by means of the factor 0.1374, and calculate the percentage of free sulphur.

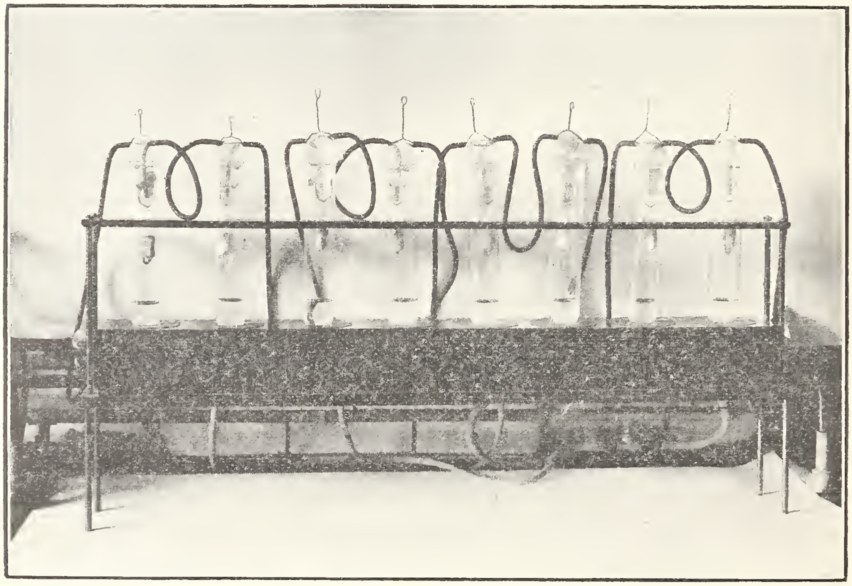


FIG. 31.—*Acetone extraction bath*

(12) *Total Sulphur.*—Place 0.5 gram of rubber in a porcelain crucible of about 100 cc capacity. Add 20 cc of the nitric acid-bromine mixture (paragraph 7), cover the crucible with a watch glass, and allow to stand for one hour. Heat very carefully for an hour, remove the cover, rinsing it with a little distilled water,

and evaporate to dryness. Add 5 grams of fusion mixture (paragraph 8) and 3 to 4 cc of distilled water. Digest for a few minutes, and then spread the mixture halfway up the side of the crucible to facilitate drying. Dry on a steam bath or hot plate. Fuse the mixture, using a sulphur-free flame (see Fig. 32), until all the organic matter has been destroyed and the melt is quite soft. Allow to cool, place the crucible in a 600-cc beaker, and cover with distilled water. Digest three or four hours on the steam bath. Filter into an 800-cc beaker, washing thoroughly with hot water. The total volume should be about 500 cc. Add 7 to 8 cc concentrated hydrochloric acid to the filtrate, and heat on the steam bath. Test the solution for acidity with congo paper, add 10 cc of 10 per cent barium chloride solution, and allow to stand overnight. Filter off the barium sulphate as before. Calculate to percentage of sulphur present.

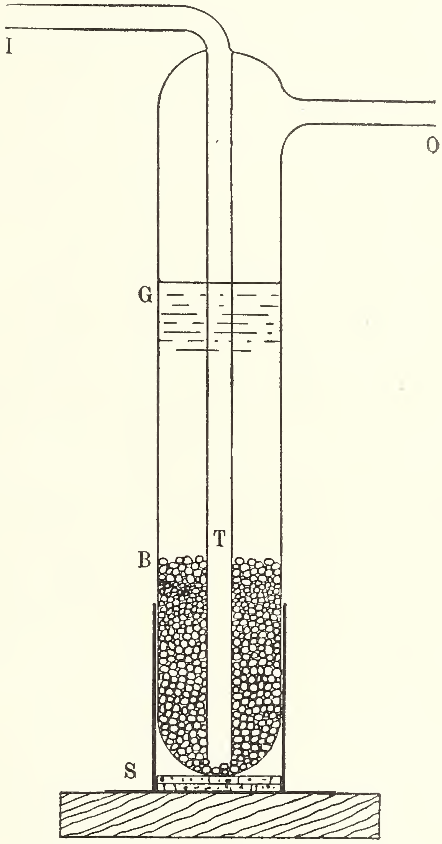


FIG. 32.—*Gasolene burner for sulphur determinations*[7]

(13) *Ash.*—Wrap a 1-gram sample in an 11-cm 590-S. & S. filter paper, and after extracting with acetone for four hours transfer to a medium-sized porcelain crucible and ignite at the lowest possible temperature; cool and weigh.

(14) *Sulphur in Ash.*—Add a few drops of concentrated nitric acid to the ash (paragraph 13), stir with a small glass rod and

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[7] C. E. Waters, J. Ind. and Eng. Chem., 5 (1913), p. 853.

evaporate off the excess acid on the steam bath. Add 5 grams of fusion mixture (paragraph 8) and heat until fused. When cool, place the crucible in a 400-cc beaker, cover with water, and heat on the steam bath for two or three hours. Filter into a 600-cc beaker (reserve the insoluble residue for testing according to paragraph 15), add 7 to 8 cc concentrated hydrochloric acid to the filtrate, cover, and heat to boiling on the steam bath. Add 10 cc of 10 per cent barium chloride solution, and allow to stand overnight. Treat the barium sulphate precipitate as under paragraph 11. Calculate to sulphur by the factor 0.1374.

(15) *Barytes.*—In the event that the total sulphur is limited by specification and barytes is permitted as a filler, the latter must be determined, since the sulphur present in this mineral must be deducted from the total sulphur. The barytes is calculated from the barium in the ash determined as follows: Filter off the insoluble matter after the fusion and extraction in paragraph 14, wash back into the original beaker with hot water, add 5 cc of 10 per cent hydrochloric acid, and heat the solution on the steam bath until as much as possible is dissolved. Filter through the same filter as before, washing thoroughly with hot water. Nearly neutralize the solution with sodium carbonate, leaving it slightly acid. Saturate the solution with hydrogen sulphide, and when the lead sulphide has settled filter into a 400-cc beaker and wash thoroughly. The total volume should not be over 200 cc. Cover the beaker containing the filtrate, heat to boiling, and add 10 cc of 10 per cent sulphuric acid. Allow the precipitate to stand overnight. Filter off the barium sulphate as directed in paragraph 11. Calculate the percentage of barytes. Then calculate the percentage of sulphur in the barytes by the factor 0.1374.

(16) *Calculations.*—(*a*) Subtract the "free sulphur" from the "acetone extract uncorrected," and report the difference as "acetone extract corrected." (*b*) Subtract the sulphur in the ash from the ash as determined in paragraph 13, and report 'ash, sulphur-free." (*c*) Subtract from the total sulphur determined according to paragraph 12, the percentage of sulphur present as barytes, if the latter determination has been made (see paragraph 15), and report the difference as "total sulphur

corrected." Then add the sulphur so deducted to the ash, in this case reporting the latter simply as "ash corrected." In other words, only the sulphur other than that in barytes will be deducted from the ash when the total sulphur is corrected for barytes. (*d*) Subtract from 100 per cent the sum of the "acetone extract corrected," total sulphur (corrected or not, as the case may be), and ash (sulphur-free, or corrected for sulphur other than barytes), and call the remainder "rubber by difference." (*e*) Divide the "acetone extract corrected" by the sum of the "acetone extract corrected" and the "rubber by difference," and call the result "ratio, acetone extract to rubber." It will be simpler to express the results in percentages. When new rubber only is used this will give the percentage of acetone-soluble matter in the rubber.

(17) *Specific Gravity.*—Make this determination in a pycnometer, using about 5 grams of rubber cut into small strips, taking care to avoid having air bubbles adhering to the rubber. Do not use a ground sample for this determination, since it is intended to determine the specific gravity of the compound as a whole. Aside from the difficulty of completely removing air bubbles, the specific gravity of a sample which is at all porous will be, after grinding, higher than when this is determined on strips. Calculate the specific gravity on the basis of water at 15° C as 1.00.

(18) *Alcoholic-Potash Extract.*—Fire hose, tested according to the National Board of Fire Underwriters' specifications, calls for an alcoholic-potash extraction. It is performed on the dried rubber remaining after the acetone extraction. The complete method will be given under paragraph 28.

(*d*) ANALYSIS OF 30 PER CENT PARA INSULATION.

(19) *General.*—The determinations to be made on high-grade insulation compounds are acetone extract, unsaponifiable matter, waxy hydrocarbons, free sulphur, ash, and total sulphur, and sometimes alcoholic-potash and chloroform extracts.

(20) *Acetone Extract.*—Determine as under paragraph 10.

(21) *Unsaponifiable Matter.*—Add to the acetone extract (paragraph 20) 50 cc normal alcoholic potash (paragraph 6), heat on steam bath under a reflux condenser for two hours; remove the

condenser and evaporate to dryness. Transfer to a separatory funnel, using about 100 cc water; add 25 cc ether, and shake. Allow the two layers to separate thoroughly, then draw off the water layer. Continue the extraction of the water layer with fresh portions of ether until the ether will no longer remove any unsaponifiable matter; unite the ethereal layers, and wash with distilled water, adding the first wash water to the extracted aqueous layer. This aqueous solution is reserved for the free sulphur determination (paragraph 23). Transfer the ether to a tared Erlenmeyer flask, distil off the ether, dry at 90° to 95° C; cool and weigh.

(22) *Waxy Hydrocarbons.*—To the unsaponifiable matter (paragraph 21) add 50 cc absolute alcohol and heat on the steam bath for one-half hour. Place the flask in a mixture of ice and salt and let stand for one hour. Filter off the separated waxy hydrocarbons, using S. & S. 589 blue-ribbon filter paper, and applying a gentle suction. Wash with alcohol which has been cooled in an ice-salt mixture. The funnel should be surrounded by a freezing mixture in order that the temperature may not rise during filtration. Dissolve the precipitate from the filter paper with hot chloroform, catching the solution in a weighed 100 to 150 cc beaker. Wash the flask with hot chloroform and add the washings to the same beaker, in order to include any insoluble matter adhering to the walls of the flask. Evaporate off the solvent, dry the residue at 90° to 95° C, cool and weigh.

(23) *Free Sulphur.*—Transfer the aqueous solution (paragraph 21) to a 250-cc beaker, and heat on the steam bath until the ether has been removed. Add 25 cc bromine water, heat one hour, add 5 cc concentrated hydrochloric acid, and heat until the excess of bromine has been driven off. (Test for acidity with congo paper; the amount of acid specified is sufficient if instructions are followed exactly, and a large excess of acid is to be avoided.) Filter into a 250-cc beaker, add 10 cc 10 per cent barium chloride solution and finish the determination as under paragraph 11.

(24) *Ash.*—Proceed as under paragraphs 13 and 14.

(25) *Total Sulphur.*—Proceed as under paragraph 12. There will be no correction for barytes.

(26) *Calculations.*—(*a*) Subtract the sum of the "free sulphur" and "waxy hydrocarbons" from the "acetone extract uncorrected," and report the difference as "acetone extract corrected." (*b*) Subtract from 100 per cent the sum of the "acetone extract corrected," "waxy hydrocarbons," "ash sulphur-free," and "total sulphur," and report the result as "rubber by difference." (*c*) Divide the "acetone extract corrected" by the sum of the "acetone extract corrected" and the "rubber by difference," and report the results under "ratio, acetone extract to rubber," as under paragraph 16 (*e*).

(27) *Chloroform Extract.*—Without removing the adhering acetone from the rubber (paragraph 20) extract with chloroform for four hours. Evaporate off the solvent in a weighed flask or beaker, dry at 90° to 95° C, cool and weigh. Reserve the rubber for the alcoholic-potash determination.

(28) *Alcoholic-Potash Extract.*—Dry the rubber (paragraphs 10, 18, and 27) at about 50° to 60° C, transfer to a 200-cc Erlenmeyer flash, add 50 cc alcoholic-potash solution, and heat under a reflux condenser for four hours. Filter through a folded filter into a 250-cc beaker, washing with 50 cc of 95 per cent alcohol, and then 50 cc of boiling water. Evaporate the filtrate to dryness. Transfer the residue to a separatory funnel, using about 75 cc of distilled water. Add a few drops of methyl orange, and acidify the solution with 10 per cent hydrochloric acid. Extract with four portions of ether, 25 cc each, unless the fourth portion should be colored, when the extraction should be continued until no further quantity can be extracted. Unite the ether fractions, wash thoroughly with distilled water, and evaporate the ether in in a weighed beaker. Dry at 90° to 95° C, cool and weigh.

4. JOINT RUBBER INSULATION COMMITTEE ANALYSIS

On October 15, 1913, the Joint Rubber Insulation Committee adopted a tentative method of analysis and specification for 30 per cent Hevea insulation compounds. Their report was published in the Proceedings of the American Institute of Electrical Engineers, **33** (January, 1914), pages 121 to 140, and the Journal of Industrial and Engineering Chemistry, **6** (1914), pages 75 to 82.

The Analytical Committee of the Rubber Section of the American Chemical Society investigated this method of analysis, and as a result of its work made the following recommendations:

1. The results of our investigations have shown that the determinations of acetone extract, free sulphur, total waxy hydrocarbons, and total sulphur are sufficiently accurate and reliable to warrant our indorsement.

2. The results of our investigations have shown that the determination of fillers is inaccurate and unreliable and therefore the calculation of the amount of rubber as prescribed by this procedure is equally inaccurate and unreliable.

3. The results of our investigations have shown that the contributing steps for the division of resins into saponifiable and unsaponifiable resins are inaccurate and unreliable; therefore, the sum of the two should be reported as resins present and no division of resins indicated.

These recommendations were presented to the Rubber Section of the American Chemical Society at Cincinnati on April 8, 1914, and published in the Journal of Industrial and Engineering Chemistry, 6 (1914), page 514.

The Joint Rubber Insulation Committee (Journal of Industrial and Engineering Chemistry, 6 (1914), page 515) admitted the inaccuracy of the method for fillers. The division of the resins, as stated in the third recommendation, is still a matter of controversy.

In order that the public may have the benefit of whatever merit it may possess, the analytical procedure is given below. Its publication in this circular, however, must not be taken as equivalent to official indorsement by the Government or even by the Bureau itself, and the fact should not be lost sight of that the recommendations of the report are not final. It was not thought desirable to include the explanation of the analytical procedure, since the essential information contained therein is included in the explanation of the Bureau of Standards methods. The specification and the explanation of the specification are given since they are intended to accompany the analytical procedure, and because of the general interest in the subject of specifications for rubber goods.

(*a*) ANALYTICAL PROCEDURE.—

(1) *Object of the Analysis.*—The object of this procedure of analysis is to determine whether rubber compounds comply chemically with the accompanying specification, which is intended to secure compounds containing 30 per cent of the best Hevea rubber and mineral fillers.

(2) *Outline of Procedure.*—The general procedure is shown by the accompanying diagram (Fig. 33), which gives an outline of the separations to be affected by acetone and chloroform extractions, and saponification with alcoholic potash.

(3) *General.*—Make the analysis upon the insulation after vulcanization, and whenever possible before the saturation of the braid. Wipe the insulation thoroughly with a damp cloth to remove any adhering material, but do not remove waxy hydrocarbons from the surface.

(4) If, however, a saturated braided sample must be used, remove the braid and sandpaper the insulation to a depth of at least five one-thousandths of an inch and wipe with a damp cloth. In such cases report the condition of the sample.

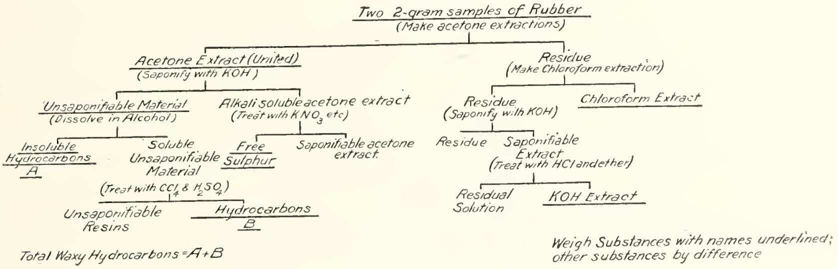


FIG. 33.—*Rubber analysis. Outline of method exclusive of fillers and total sulphur determinations*

(5) Perform all determinations in duplicate and take the average value arbitrarily as the true value. Duplicate determinations must check within the limits specified.

(6) Make blanks on all determinations and deduct the results accordingly.

(7) *Sample.*—Remove the insulation entirely from sufficient wire to give a sample weighing about 25 grams. Cut this into small strips and grind slowly in either a No. 0 Enterprise coffee mill or a mill such as shown by the accompanying diagram (Fig. 34). Adjust the grinder so that not more than 20 per cent will pass through a 40-mesh sieve. Sift all the material through a 20-mesh sieve, regrinding what is retained on the sieve until the entire sample has passed through. The wires of the sieves shall

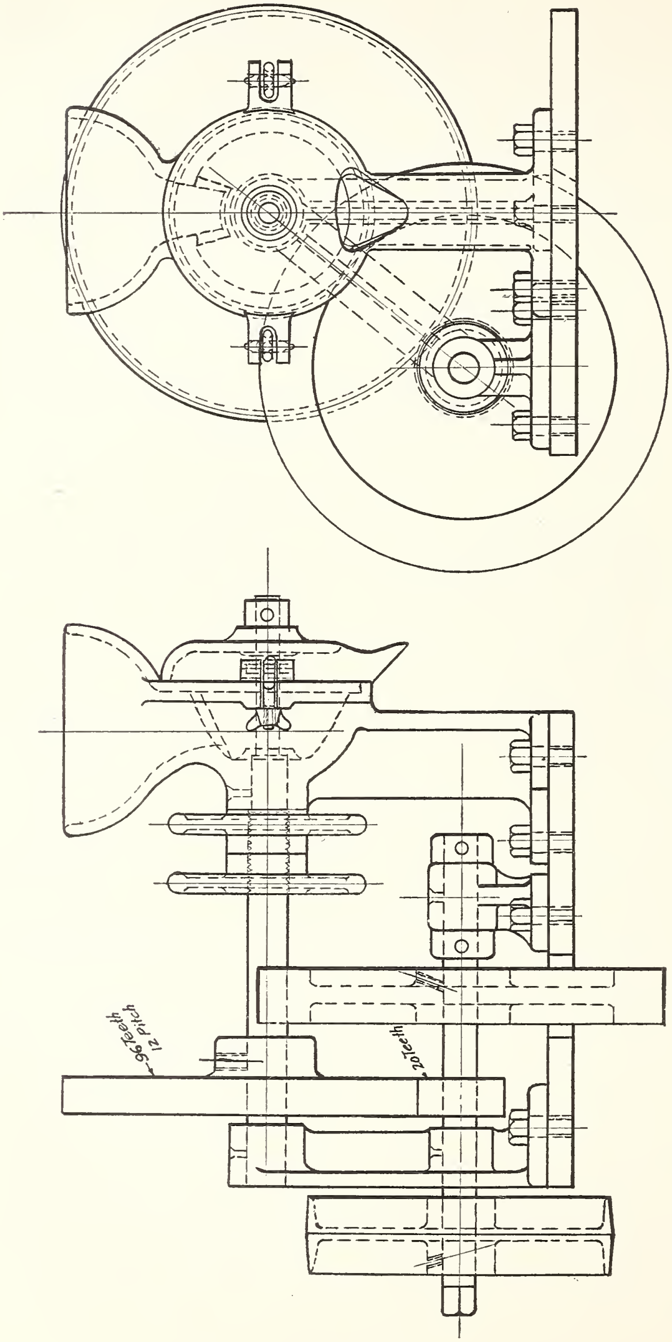


Fig. 34.—*Rubber grinder*

be evenly spaced in both directions and shall be of 0.016 and 0.010 inch diameter in the 20 and 40 mesh sieves, respectively. Remove with a strong magnet any metal that may have come from the grinder and thoroughly mix the sample.

(8) *Extraction Apparatus.*—The extraction apparatus shall conform with the accompanying diagram (Fig. 35). It shall be heated so that the period of filling an empty siphon cup with acetone and completely emptying it will be between two and one-half and three and one-half minutes.

(9) *Preparation of Reagents.*—Acetone shall be freshly distilled over anhydrous potassium carbonate, using the fraction 56° to 57° C.

(10) Alcoholic-potash solution shall be of normal strength and shall be made freshly, dissolving the proper amount of potassium hydroxide (purified by alcohol) in 95 per cent alcohol which has previously been distilled over potassium hydroxide. The solution shall be allowed to stand for 24 hours and only the clear liquid used.

(11) Ether shall be washed with three successive portions of distilled water and distilled, using the fraction 34° to 36° C.

(12) Chloroform shall be pure and freshly distilled.

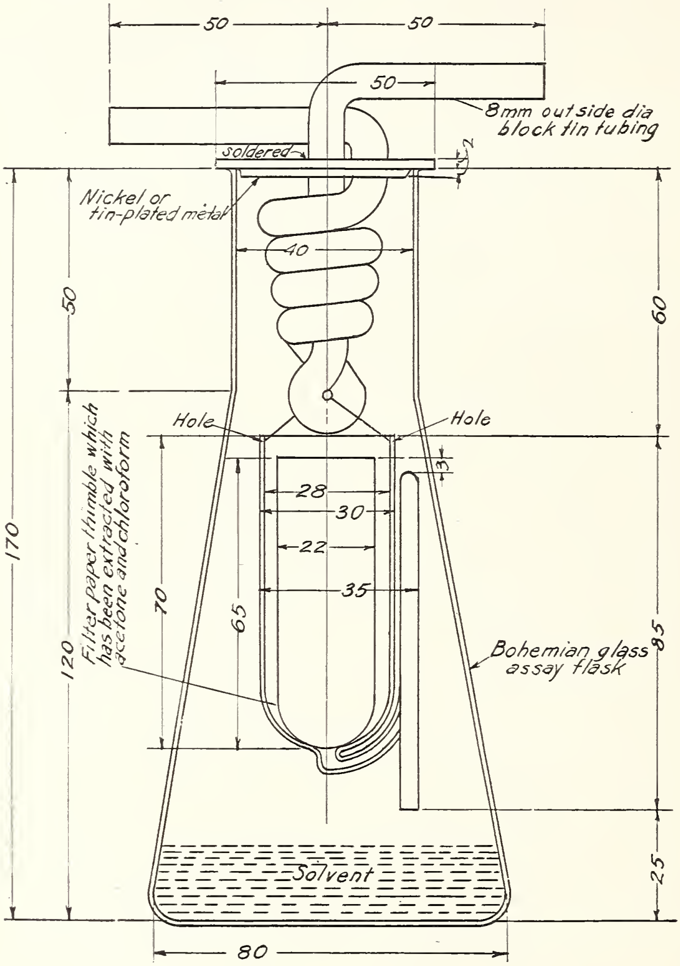
(13) Carbon tetrachloride shall be pure and freshly distilled.

(14) Reagents not otherwise specified shall be chemically pure.

(15) *Acetone Extraction.*—Extract continuously with 60 cc acetone for 8 hours two 2-gram samples that have been prepared within 24 hours. Unite the extracts in a weighed flask, using hot chloroform to rinse the flasks. Distill off the reagents and dry the flask and contents for 4 hours at 95° to 100° C. Desiccate until cool and weigh. Continue to dry for 2-hour periods until constant weight is obtained. In drying, place the flask on its side, but at a sufficient angle from the horizontal, so that the extract does not appreciably run down the side of the flask.

(16) *Unsaponifiable Material.*—Add to the acetone extract 50 cc alcoholic potash solution, boil under a reflux condenser for 2 hours, and evaporate to dryness, removing all alcohol. Add 10 cc water and 20 cc ether; heat until the wax, etc., are in solution, cool, transfer to a separatory funnel, wash out the flask with warm water, and then cool, finally with two 20-cc portions of ether.

The water volume should be 100 cc and the ether at least 40 cc. Shake vigorously for two minutes, and allow the solutions to separate thoroughly. Draw off the aqueous solution into a second funnel, leaving in the first funnel the ethereal solution and any flocculent material that may be present. Again rinse the flask with 20 cc ether and add it to the aqueous solution; shake vigor-



All dimensions in millimeters

FIG. 35.—*Extraction apparatus*

ously for two minutes, and when separated draw off the aqueous solution and unite in the first funnel the ethereal solutions and any flocculent material. Repeat, shaking with 20-cc portions of ether until the extraction is complete, using at least 120 cc ether. Wash the flask and the funnel from which the ethereal solution has been taken with water until they are free from alkali, subsequently using this wash water to wash the ethereal solution. Continue washing with water until it has been washed twice after it shows no alkaline reaction. Retain with the ethereal solution any flocculent material. Filter the ethereal solution from the flocculent material, through a small pellet of extracted cotton, into a weighed flask, washing first with ether and subsequently with hot chloroform, using this to rinse the original flask and both separatory funnels. Evaporate the solvents and dry the extract to constant weight at 95° to 100° C; desiccate until cool and weigh.

(17) *Hydrocarbons A.*—Add 50 cc absolute alcohol to the unsaponifiable material and warm until solution is as complete as possible. Cool the solution to $-4°$ or $-5°$ C and maintain at this temperature for one hour by packing the flask in a mixture of ice and salt. Filter out the waxy hydrocarbons, using a funnel packed with ice and salt and applying suction if necessary. Wash the flask and filter with 25 cc of 95 per cent alcohol, which has been previously cooled in the same temperature. Catch the filtrate in a flask which is afterwards cooled to $-4°$ or $-5°$ C to make sure that all possible waxy hydrocarbons have been removed, and refilter if necessary. Dissolve the residue on the filter paper with hot chloroform into the original flask. Evaporate the chloroform and dry the flask to constant weight at 95° to 100° C; cool in a desiccator and weigh.

(18) *Hydrocarbons B.*—Evaporate the alcohol from the flask containing the alcohol soluble unsaponifiable material, add 25 cc carbon tetrachloride and transfer to a separatory funnel. Shake with concentrated sulphuric acid, drain off the discolored acid and repeat with fresh portions of acid until there is no longer any discoloration. After drawing off all the acid, wash the carbon tetrachloride solution with repeated portions of water until all traces of acid are removed. Transfer the carbon tetrachloride

solution to a weighed flask; evaporate off the solvent and dry the flask to constant weight at 95° to 100° C. Cool in a desiccator and weigh.

(19) *Free Sulphur.*—Add 2 grams potassium nitrate to the aqueous solution and washings from the ethereal separation of the unsaponified material. Evaporate to dryness in a silver or nickel dish and heat to quiet fusion, avoiding contamination with sulphur fumes. Transfer with water to an evaporating dish, acidify with hydrochloric acid, evaporate to dryness, and dehydrate silica. Add 2 cc hydrochloric acid, take up in water, filter and wash, making a volume of 200 cc. Heat to boiling and add slowly a slight excess of hot 10 per cent barium chloride solution. Allow to stand overnight, filter, wash, ignite, weigh the barium sulphate and calculate to sulphur.

(20) *Definition of Terms Describing Components of Acetone Extract.*—The difference between the acetone extract and the free sulphur shall be called the organic extract.

(21) The difference between the organic extract and the unsaponifiable material shall be called the saponifiable acetone extract.

(22) The sum of the hydrocarbons A and B shall be called the total waxy hydrocarbons.

(23) The difference between the unsaponifiable material and the waxy hydrocarbons shall be called unsaponifiable resins.

(24) *Chloroform Extraction.*—Extract continuously the residue from one of the acetone extractions (without necessarily removing the acetone that may be on it) for four hours with 60 cc chloroform, using a weighed flask. Distil off the solvent and dry the flask and contents for two hours at 95° to 100° C. Desiccate until cool and weigh. Continue to dry for one-hour periods until constant weight is obtained. In drying, place the flask on its side, but at a sufficient angle from the horizontal, so that the extract does not appreciably run down the side of the flask. (If it is needful to wait after the acetone extraction before starting the chloroform extraction, the sample must be kept in a vacuum of at least 50 mm mercury.)

(25) *Alcoholic-Potash Extraction.*—Dry the residue from the chloroform extraction at 50° to 60° C, put into a 200-cc Erlenmeyer flask with 50 cc alcoholic-potash solution and boil for four hours under a reflux condenser. Filter the solution into a beaker and wash twice, using each time 25 cc hot absolute alcohol, and then wash thoroughly with hot water. Evaporate the solution to approximate dryness, take up in warm water, and transfer to a separatory funnel. Acidify with 15 cc 5N hydrochloric acid, using this to rinse the beaker. Add sufficient water to make the bulk of the solution 100 cc. When cool add 40 cc ether, using it to rinse the beaker in 20-cc portions. Shake the aqueous and ethereal solutions thoroughly. After complete separation, draw off the aqueous solution and treat in another separatory funnel, with a fresh 20-cc portion of ether. Continue to shake the aqueous solution with fresh portions of ether until a colorless portion has been obtained, then shake out twice more. Unite the ethereal solutions and wash with successive additions of water, continuing twice after the water shows no acid reaction. Filter through a plug of extracted cotton into a tared flask, wash the filter and funnel with ether, evaporate the ether without boiling and dry the residue to constant weight at 95° to 100° C. Cool in a desiccator and weigh.

(26) *Fillers.*—Extract a 1-gram sample with acetone for five hours. Transfer the residue to a tall-lipped 200-cc beaker, add 40 cc terebene and 20 cc xylol, and heat on an oil bath at 105° to 110° C for about 20 hours, or until the bulk of the fillers settle promptly after stirring. Occasional stirring will aid the solution. Allow the beaker to stand until the fillers and undissolved residue have settled thoroughly and decant the supernatant solution into a beaker. Add to the undisturbed residue 30 cc terebene; heat several hours, allow to settle, decant, unite the decanted solutions, and repeat this treatment as long as there is any indication of rubber being present. Continue to heat the decanted solutions during the further treatment of the undissolved residue and filter them through a tared filter paper. This filter paper must be of close texture and shall have been washed with terebene, alcohol, and acetone. The tare filter shall be treated with the same

solvents and dried in the same manner throughout the analysis as the filter containing the residue. Weigh all filter papers in weighing bottles of sufficient size to take them without folding. Refilter if mineral matter runs through. Wash the beaker that contained the decanted solutions and the filter paper with benzol, using a second beaker to catch the filtrate. Add benzol to the beaker containing the residue, heat, and after settling decant, repeating this treatment with benzol until it is thoroughly washed. Filter and wash well with benzol. Wash in the same manner both beakers with hot alcohol, and then transfer the residues to the filter paper, using hot alcohol and an acetone-extracted policeman. Wash finally with acetone. Dry in air at 95° to 100° C, and weigh. Again wash the filter paper and contents with benzol and alcohol, dry, weigh, and repeat this treatment until constant weight is obtained. Evaporate all the filtrates and washings, transfer to a porcelain dish, burn off, and weigh. Add this amount to the fillers found above. If this ash is greater than 1 per cent, the entire determination shall be repeated. Subtract 0.5 per cent as an arbitrary value for the amount of organic matter from the rubber retained with the fillers.

(27) *Sulphur in Fillers.*—Transfer the fillers from the filter paper into an iron crucible; burn the filter paper and add the ash to the crucible. Add the total sulphur flux and proceed with the determination of sulphur as in "Total sulphur" below. Subtract the percentage of sulphur found from the percentage of fillers to determine the percentage of fillers free from sulphur.

(28) *Total Sulphur.*—Mix a 0.5-gram sample with 4 grams sodium peroxide and 6 grams potassium carbonate in a dry 15-cc iron crucible. Cover and heat gradually until the mixture fuses, proceeding cautiously, as rapid heating will cause an explosion, and then bring to quiet fusion for 15 to 20 minutes. Apply the heat so as to avoid contamination with sulphur fumes. Rotate the crucible while the melt solidifies. When cool, put crucible and cover into a casserole containing 200 cc of water; add 5 to 10 cc bromine water and boil until the melt is dissolved. Allow the precipitate to settle, decant the liquid through a thick filter, and wash the residue with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and dehydrate silica; add 2 cc

concentrated hydrochloric acid, take up in water, filter, and wash, making the total volume about 400 cc. Heat to boiling and add slowly a slight excess of hot 10 per cent barium chloride solution. Allow to stand overnight, filter, wash, ignite, weigh the barium sulphate, and calculate to sulphur.

(29) *Specific Gravity.*—The specific gravity shall be the ratio of the weight of a given volume of the rubber to the weight of an equal volume of water, both at 20° C. Cut strips of the largest applicable size from the conductor and use about 5 grams for the sample. Determine the specific gravity in the usual manner by means of a specific-gravity bottle. Care must be taken that no air bubbles adhere to the sample.

(30) *Checks.*—Specific-gravity determinations shall check within 0.01. The other duplicate determinations shall check within the following limits expressed as percentages of the original sample:

	Check
Acetone extract	0.10
Saponifiable acetone extract	.10
Unsaponifiable resins	.10
Waxy hydrocarbons	.10
Free sulphur	.05
Chloroform extract	.10
Alcoholic potash extract	.10
Fillers, free from sulphur	.50
Total sulphur	.10

(31) *Interpretation.*—The rubber shall be considered to be the difference between 100 and the sum of the waxy hydrocarbons, total sulphur, and the fillers (free from sulphur), expressed as percentages. If the chloroform extract is over 3 per cent of the rubber so calculated, subtract the excess from the rubber. If the alcoholic potash extract is over 1.8 per cent of the rubber, as first calculated, subtract this excess also from the rubber.

(32) *Carbon and Red Lead.*—Heat about 1 gram of the sample with 30 cc concentrated nitric acid and 15 cc water. A black insoluble residue indicates the presence of carbon.

When the rubber is dissolved in the fillers determination, the absence of any red particles indicates the absence of red lead. If red particles are present, dissolve another sample by the same method as the fillers (sec. 26), filter the solution into a Gooch crucible and wash thoroughly. Remove the felt and residue to a distilling flask, add hydrochloric acid, and distill over the chlorine liberated by the lead peroxide, absorbing the gas in a solution of potassium iodide and starch. Not more than 0.1 cc $\frac{N}{10}$ thiosulphate shall be required to titrate the iodine liberated.

(*b*) SPECIFICATION FOR 30-PER CENT HEVEA RUBBER COMPOUND.—(1) A 30-per cent fine Para or smoked first-latex Hevea rubber compound with mineral base shall be furnished. It shall contain only the following ingredients: Rubber, sulphur, inorganic mineral matter, refined solid paraffin or ceresin.

(2) It shall not contain either red lead or carbon.

(3) The vulcanized compound shall conform to the following requirements when tested by the procedure which forms a part of this specification.

(*a*) Results to be expressed as percentages by weight of the whole sample:

	Maximum	Minimum
Rubber (see sec. 31, "Analytical procedure")	33	30
Waxy hydrocarbons	4	....
Free sulphur	0.7	....

(*b*) Results to be taken between the limits given in proportion to the percentage by weight of rubber found:

	Maximum	Minimum
Limits allowed for 30 per cent rubber compound:		
Saponifiable acetone extract	1.35	0.55
Unsaponifiable resins	.45	....
Chloroform extract	.90	....
Alcoholic potash extract	.55	....
Total sulphur (see note 3)	2.10	....
Specific gravity	....	1.75
Limits allowed for 33 per cent rubber compound:		
Saponifiable acetone extract	1.50	.60
Unsaponifiable resins	.50	....
Chloroform extract	1.00	....
Alcoholic potash extract	.60	....
Total sulphur (see note 3)	2.30	....
Specific gravity	....	1.67

(4) The acetone solution shall not fluoresce.

(5) The acetone extract (60 cc) shall be not darker than a light straw color.

(6) Hydrocarbons shall be solid, waxy, and not darker than a light brown.

(7) Chloroform extract (60 cc) shall be not darker than a straw color.

(8) Failure to meet any requirement of this specification will be considered sufficient cause for rejection.

Note 1.—Contamination of the compound, such as by the use of impregnated tapes, will not excuse the manufacturer from conforming to this specification.

Note 2.—This specification shall be supplemented by appropriate clauses relating to tensile strength, elasticity, insulation resistance, and dielectric strength.

Note 3.—The limit on total sulphur may be omitted at the option of the purchaser. (See explanation of specification.)

(*c*) EXPLANATION OF SPECIFICATION—

(1) Experience has shown that compounds which upon analysis show the characteristics of good Hevea rubber may be relied upon to be more permanent than those made of rubber of other grades. It is not affirmed by the committee that a compound which conforms with this specification is necessarily permanent or that a better compound can not be made, but it is believed that enforcement of the specification will limit the use of inferior materials, and that it will put the manufacturers more nearly upon an equality of endeavor, where they can use their experience to obtain the best results. Used in connection with the analytical procedure, the specification will enable purchasers to order a good compound and to ascertain with a greater certainty than heretofore whether the material received represents the compound specified.

(2) The term "Hevea" applied to rubber means rubber from the *Hevea brasiliensis* tree, whether wild or cultivated, and regardless of the locality in which it has been grown. Para rubber is Hevea rubber which has been shipped from the port of Para, Brazil, and comes in several grades. Smoked first-latex Hevea

rubber is a high-grade plantation rubber, which is collected prime and consists entirely of rubber which has risen in the settling vats. It is coagulated chemically and smoked in order to give it a hard cure, which insures the greatest durability. The rubber required by this specification should be Hevea rubber of good quality, such as fine Para or smoked first latex.

(3) Carbon is excluded because it is considered, by some purchasers, to be deleterious.

(4) Red lead is excluded because of the possibilities of its deleterious effects on the rubber.

(5) Ozokerite is prohibited because the acetone extract obtainable from it interferes with the separation of the acetone extract obtainable from the rubber, thereby vitiating the assay of the rubber extract. This prohibition is unimportant to the manufacturers, as ceresin, which is permitted, is the essential constituent of ozokerite.

(6) An upper limit is placed upon the rubber in order to prevent the attainment of electrical and mechanical strength by the use of an extra quantity of inferior rubber whose lasting qualities might not be satisfactory.

(7) The hydrocarbons are limited, owing to their tendency to separate from the compound and thus possibly cause porosity.

(8) The free sulphur is limited because an excessive amount may by deleterious.

(9) The maximum limit on the saponifiable acetone extract is to prevent the use of raw or reclaimed rubber with high acetone saponifiable extract. The minimum limit assists in forcing the use of Hevea rubber, since it is characteristic of the acetone extract from Hevea rubber to be largely saponifiable.

(10) The unsaponifiable resins are limited because a low proportion of unsaponifiable resins is characteristic of Hevea rubber. A high result might be due to the presence of reclaimed rubber.

(11) The chloroform extract is limited, first, to prevent the use of bituminous substances, and, second, to limit depolymerized and undercured rubber.

(12) The alcoholic potash extract is limited to prevent the use of saponifiable rubber substitutes.

(13) The specific gravity is limited to reconcile the specification of ingredients by weight with the practice of purchasing material by volume.

(14) Fluorescence of the acetone solution is prohibited as it indicates the presence of mineral oils.

(15) The color of the acetone extract is specified to conform with the normal color of the extracts from Hevea rubber. A darker color indicates adulteration or an inferior grade of rubber.

(16) The hydrocarbons are required to be solid in order to prevent the use of oils and paraffin of low melting point. The shade required is that obtained from paraffin wax or ceresine. If hydrocarbons B are liquid, this would indicate reclaimed rubber softened with mineral oil, or a poor grade of paraffin.

(17) The color of the chloroform extract is specified to conform with the color of dissolved gum in minute quantities. The presence of bituminous substances would be indicated by a brown or black color.

(18) It would be desirable that the sulphur of vulcanization be limited to exclude reclaimed rubber, which contains the sulphur of its previous vulcanization, but the committee has not yet developed an acceptable method for determining this quantity. It is therefore confronted with the choice of either placing a limit on the total sulphur or giving up the attempt to exclude shoddy by sulphur limitation. Option is therefore given to the purchaser to insert or omit the limit on total sulphur. Such insertion will at times exclude reclaimed rubber, and the committee believes it possible to make a suitable compound with this limitation. The committee thinks that a sulphur limit positively excluding reclaimed rubber would place too great a hardship, in other ways, on the manufacturers. Where the specification is used with no total sulphur limit, the use of many kinds of, or much, reclaimed rubber will be guarded against by the limits of the various components of the acetone extract. When the limitation on total sulphur is omitted, sulphur-bearing fillers, which possess certain advantages, may be used.

(19) This specification should be supplemented by appropriate elasticity and tensile strength tests, in order to add to the assur-

ance that good rubber has been used and that the vulcanization process has been properly carried out; also by appropriate electric stress and resistance tests, to assure proper insulating qualities and homogeneity of structure. The exact values of the limits for these tests will depend upon the use to which the material is to be put.

V. BIBLIOGRAPHY

This circular, as its title indicates, is concerned chiefly with the problems connected with the testing of rubber goods. There will be many who are interested in other phases of the rubber industry, and for their benefit a partial list of publications is given below.

PUBLICATIONS OF THE BUREAU OF STANDARDS

Bulletin Reprint No. 174.
Technologic Papers Nos. 35 and 45.

BOOKS

The Chemistry of India Rubber, by Carl Otto Weber. Charles Griffin & Co. (Ltd.,) London, 1902.
Rubber, by Philip Schidrowitz. Methuen & Co. (Ltd.), London, 1911.
Rubber Tires, by Henry C. Pearson. The India Rubber Publishing Co., New York, 1906.
Crude Rubber and Compounding Ingredients, by Henry C. Pearson. The India Rubber Publishing Co., New York, 1899.
India Rubber Laboratory Practice, by W. A. Caspari. Macmillan & Co. (Ltd.), London, 1914.
Der Kautschuk und seine Prüfung, by F. W. Hinrichsen and K. Memmler. S. Hirzel, Leipzig, 1910.
Die Analyse des Kautschuks, etc., by Rudolf Ditmar. A. Hartleben, Leipzig, 1909.
The Manufacture of Rubber Goods, by Adolf Heil and W. Esch, translation by Edward W. Lewis. Charles Griffin & Co. (Ltd.), London, 1909.
The Chemistry of Rubber, by B. D. Porritt. D. Van Nostrand Co., New York, 1914.
The Chemistry of the Rubber Industry, by Harold E. Potts. Constable & Co. (Ltd.), London, 1912.

PERIODICALS

DEVOTED SOLELY TO THE INTERESTS OF THE RUBBER INDUSTRY

India Rubber World.
India Rubber Journal.
Gummi Zeitung.
Le Caoutchouc et la Gutta Percha.

HAVING OCCASIONAL ARTICLES ON RUBBER

Journal of Industrial and Engineering Chemistry.
Chemical Abstracts.
Journal of the Society of Chemical Industry.
The Analyst.
Kolloid-Zeitschrift.

VI. REGULATIONS REGARDING TESTS

The Bureau has been for some time testing rubber for the various Government departments and is prepared to perform such service for the general public in special cases. The Bureau will also be glad to cooperate with investigators, manufacturers, and others not only in executing tests, but also, on request, in furnishing any information at its disposal concerning methods of testing rubber.

FEES.—The Bureau is not yet in position to adopt a complete schedule of fees, but a reasonable charge will be made in each case, depending upon the nature of the test. A few of the more usual physical tests will entail a fee, as shown in the following schedule:

SCHEDULE NO. 115

Physical Tests of Rubber

(*a*) Rubber water hose, suction hose, or fire hose	$3.00 to $5.00
(*b*) Rubber air hose	4.00 to 6.00
(*c*) Rubber air-brake hose	4.00
(*d*) Rubber steam hose	5.00 to 10.00
(*e*) Rubber dredging sleeves	5.00
(*f*) Rubber sheet packing	2.00 to 4.00
(*g*) Rubber and asbestos sheet packing	2.00 to 4.00

SCHEDULE NO. 116

Chemical Tests of Rubber

The Bureau will, in its discretion, make chemical analyses for the general public only when asked to serve as referee and in special cases. The fee in such cases will depend upon the nature and amount of work required. Estimates will be sent on receipt of full information.

Chemical analyses will be made for State and municipal governments. No fees are charged to State governments. Those for municipal governments will vary from $15 to $30 per sample, according to the amount of work required.

The Bureau reserves the right in all cases to accept or decline requests for tests, depending upon the conditions in each case.

SAMPLING.—Samples shall be taken directly from the finished material. These samples should be sealed, and marked with maker's name, date of sampling, kind of material, and sufficient other data to insure easy and complete identification. The sample should be of such size as to permit of part being taken for analysis and the remainder stored for future reference, should the occasion for such arise. Every precaution must be taken to prevent contamination of the samples by any foreign material, and they must always be stored in a cool place. The object of these precautions is to insure that the sample shall be received in exactly the condition in which it is offered by the contractor.

The following statement will show the minimum amount of material required for making the various tests, leaving a sufficiency for supplemental chemical check tests if these are needed. The amounts specified are intended to show the size of sample required on what might be considered relatively small lots. The samples should be made up of a number of pieces taken from several parts of the delivery, and from these a composite sample will be made for chemical analysis. It should be noted, however, that the pressure and steam tests on hose require a 4-foot length. Large lots should be represented by samples of corresponding size. In such cases, it may be advisable to make two or more composite samples for chemical analysis.

Physical Tests Only

Hose of all kinds, up to 3-inch diameter	2 feet
Hose of all kinds, over 3-inch diameter	1 foot
Pressure and steam tests on hose	4 feet
Packing	1 square foot
Insulated wire	4 to 6 feet
Other mechanical goods, sufficient material to give at least 6 pieces	1 inch by 6 inches

Chemical Tests Only

Hose of all kinds, up to 3-inch diameter	1 foot
Hose of all kinds, over 3-inch diameter	6 inches
Packing	¼ square foot
Insulated wire	2 to 3 feet
Other mechanical goods, sufficient material to give at least 4 ounces of rubber.	

Application for Test.—The request for test should state explicitly the specifications according to which test is to be made, and a copy of such specifications should be sent unless it is certain that the Bureau already has a copy.

Remittances.—As soon as the fee is assigned to a test, a bill is sent at once, and payment should be in advance, made by money order or check drawn to the order of the "Bureau of Standards." Results of tests are not certified until fees are paid.

Shipping Directions.—Materials should be shipped prepaid, as all transportation charges are payable by the party desiring the test. Articles should be addressed simply "Bureau of Standards, Washington, D. C."

S. W. Stratton,
Director.

Approved:
William C. Redfield,
Secretary.

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