WOOD PLASTICS AS DEVELOPED AT THE FOREST PRODUCTS LABORATORY AND THEIR FUTURE IMPORTANCE

Revised November 1941

No. R1209

UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison, Wisconsin
In Cooperation with the University of Wisconsin

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During recent years plastics have been gradually displacing metals, ceramics, and wood in the manufacture of many articles of commerce. By molding, costly machine shaping operations can be eliminated and various articles can be produced in large quantities at comparatively low cost. The expanded production of molding compositions has resulted in a substantial reduction in their price, but the cost is still too great to warrant their general use in the manufacture of large articles. More recently shortages of various metals brought about by National Defense operations have caused a great swing towards plastics to replace metals both in civilian and National Defense lines, and have caused shortages in plastics which are almost as severe as those encountered among the metals. If plastics are to continue to play a role of increasing importance in National Defence and particularly if they are to invade the field of large molded products, such as panels, instrument boards, and even automobile bodies, as is contemplated by at least one large auto manufacturer, it is evident that such a plastic must be low in cost and available in great quantities.

A survey of such prospective materials reveals that the woody portion of most vegetation is perhaps one of the most promising sources of raw material. It is abundant, widely distributed, and available at low cost because it is usually found in the form of a waste resulting from the manufacture or harvesting of some other product.

Plastic Properties

Wood alone, untreated, is somewhat plastic at elevated temperatures and by the application of sufficient pressure small particles, such as sawdust and shavings, can be pressed into a compact mass. Such pressed material is suitable for fuel briquettes, but it does not have sufficient strength for structural purposes and it rapidly disintegrates on soaking in water. However, one of the main constituents of wood, lignin, when separated from the other constituents is much more plastic and after pressing at elevated temperatures, is very resistant to water absorption. The best pressing temperature for lignin is so near the point where it begins to decompose with heat that it is necessary to use plasticizers to obtain the best results and such plasticizers improve not only the plastic properties of the lignin, but also the water resistance of the pressed product. Such a pressed product from plasticized lignin alone, although very satisfactory in water resistance is too brittle for many uses -- it needs a "filler" for improving its strength properties. This last situation is rather fortunate than otherwise, since complete removal of all the cellulosic material from wood would be an expensive process and by a comparatively simple treatment enough cellulose can be removed to render the lignin plastic, at the same time leaving enough cellulose to serve as a filler.

Several types of pretreatment have been employed in reducing the wood to a satisfactory lignin-cellulose mixture which can later, with the addition of plasticizer, be molded. Most attention has been given to pretreatments with the acid-hydrolysis and aniline-hydrolysis methods. By variation of time, temperature, and acid concentration in the acid hydrolysis pretreatment the lignin to cellulose ratio can be controlled. It has been found that this ratio very largely determines the properties of the finished material, other things being equal. A low ratio of lignin to hydrolyzed cellulose will have high strength values and low water resistance, whereas the opposite effects will be obtained in a higher lignin-cellulose ratio.

The larger part of the Laboratory's work in the preparation of wood plastics has been confined to the use of mill-run hardwood sawdust, such as from maple, oak, hickory, gum, and aspen, or to a mixture of these species. The utilization of wood waste need not be confined to the use of sawdust since hogged material from slabs, edgings, and woods waste can be successfully utilized so long as it is bark and dirt-free, nor need the waste wood be dried before processing. Although coniferous woods usually produce a material with lower strengths than the hardwoods, proper modifications of these processes may make them equally suitable for this purpose.

Plasticizers

Many plasticizing agents may be incorporated in the material after pretreatment with corresponding influences on the molding, finish, and other properties of the pressed material. The use of the proper plasticizing agents will be governed largely by the nature of the product to be produced.

Among suitable lignin plasticizers, the Forest Products Laboratory finds ketones, such as acetone, furoin, and benzoin; aldehydes, such as furfural and formaldehyde; amines, such as aniline, and ethanol amines; ethers, especially glycol ethers; esters, as of glycol, phosphoric and sulphonic acid esters of phenols and cresols, and phthalic and maleic anhydride; amides, such as urea, toluene ethyl sulphonamides, toluene sulphonamides, and cyclohexyl p-toluene sulphonamide; mixtures, such as wood-tar oils; and resins, such as phenol formaldehyde resins.

F.P.L. Acid Hydrolysis Method[1]

Conditions for a typical hydrolysis pretreatment are:

Maple (dry weight)...........	100 parts
Water.........................	250 parts
Sulphuric acid...............	3 parts
Time..........................	30 minutes
Digester pressure............	135 lb. per sq. in.

The sawdust is cooked in a rotating digester made of acid-resisting material or lined with acid resisting tile. The residue remaining in the digester is drained free of the resulting acid-sugar liquor, washed with water until neutral to litmus, and dried. The yield will be approximately 62 percent by weight of the original wood waste -- somewhat higher if lower concentrations of acid are used. This material, preferably after being ground to a particle size ranging from 40 to 100 mesh, may be subjected to hot pressing at a relatively high temperature (190° C.) with the addition of water alone. By the addition of a more specific plasticizer, such as a combination of aniline and furfural, pressing will proceed at a temperature of 150° C. with marked modifications and improvements in the properties of the product.

A molding composition may be prepared as follows:

Hydrolyzed sawdust (dry)................	100 parts
Aniline..................................	8 parts
Furfural.................................	8 parts
Zinc stearate...........................	0.5 part
Water....................................	2.0 parts

This material may then be pressed under the following conditions:

Molding temperature....................	150° C.
Molding time...........................	3 minutes
Molding pressure.......................	3,000-4,000 lb. per sq. in.
Removal temperature....................	140° C.

The product obtained is hard and dense and exhibits many of the useful properties common to the more expensive pressed materials. Values for a number of physical properties of the material are as follows:

Color - black, opaque
Finish - lustrous
Density - 1.4
Machinability - good
Tensile strength - 3,500 pounds per square inch

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[1] E. C. Sherrard et al, U. S. Patent 2,153,316.

Compressive strength - 21,000 pounds per square inch
Flexural strength - 6,000 pounds per square inch
Breakdown voltage (60 cycles) = 484 volts per mil.
Water absorption (48-hour immersion) - 2.2 percent
Impact (Izod) energy absorbed per inch of notch - 0.33 ft.-lb.
Hardness (Rockwell 1/4-inch ball, 15 kg. load) - 93-94
Distortion under heat - 251° F.

F.P.L. Aniline-Hydrolysis Process[2]

Conditions for a typical aniline-hydrolysis pretreatment are:

Maple sawdust (dry-weight)............	100 parts
Water..................................	100 parts
Aniline................................	21 parts
Time...................................	180 minutes
Digester pressure......................	160 lb. per sq. in.

The cooking is performed as described under the acid hydrolysis process. The resultant digested mass is drained free of acid liquor and washed with water until neutral to litmus. It is dried and ground to a particle size ranging between 40 and 80 mesh. The yield will approximate 95 percent by weight of the original wood waste.

A satisfactory molding composition may be prepared as follows:

Aniline-treated sawdust (dry)............	100 parts
Furfural.................................	8 parts
Water....................................	2 parts
Zinc stearate............................	0.5 part

This material is then pressed under the following conditions:

Molding temperature......................	155° C.
Molding time.............................	3 minutes
Molding pressure.........................	3,500-4,000 lb. per sq. in.
Removal temperature......................	140° C.

The molded product obtained is hard and dense, with strength values and water resistance somewhat higher than obtained from the acid-hydrolysis composition. Values for a number of physical properties pertaining to this pressed material are as follows:

Color - black, opaque
Finish - lustrous
Density - 1.40
Machinability - good
Tensile strength - 5,500 pounds per sq. in.
Compressive strength - 21,000 lb. per sq. in.
Flexural strength - 7,000 to 8,000 lb. per sq. in.

[2] E. C. Sherrard et al, U. S. Patent 2,130,783.

Breakdown voltage (60 cycles) - 420 volts per mil.
Water absorption (48-hour immersion) - 1.07 percent
Impact (Izod) energy absorbed per inch of notch - 0.44 ft.-lb.
Hardness (Rockwell, 1/4-inch ball, 15 kg. load) - 95-96
Distortion under heat - 275° F.

Both of the above described molding materials are capable of being molded in relatively thick sections (experimental moldings of more than 2 inches in thickness have been made) with almost no difficulty in obtaining a uniform cure throughout the molded piece.

They are both characterized by a relatively low mold flow and are not completely thermo-setting. That is, the molds must be cooled approximately 20° C. before removing the molded article from the mold.

Both of these characteristics can be remedied, if a high-flow, fast-curing compound is required, by the addition of 15 percent phenolic resin to the aniline-furfural plasticized powders.

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In some of the earlier work it was found that chlorinated wood[3] (1-10 percent chlorine) could be pressed at much lower temperatures and pressures. Although the treated material became highly plastic under heat and pressure, the liberation of chlorine and hydrochloric acid from the pressed product has been a limiting factor in its usefulness. Further work, no doubt, would indicate a satisfactory application of this cheap method of plasticizing wood.

General

All the above products, except those with very high lignin content, have high shock resistance, and are practically unaffected by exposure to ultraviolet light; in fact, samples exposed to ultraviolet light for more than 144 hours were blacker and shinier than before exposure. Exposure on the paint-test fence for more than 2 years shows them to have a high degree of weather resistance, the surfaces being affected less than painted or varnished wood surfaces during similar exposure.

As already noted, articles prepared from all the compositions are black. Surface modifications may be made by the application of thin wood veneer, paper, and the like, to the surfaces during the regular molding cycle, producing a very strong, shiny, hard and attractive surface. Paints, lacquers, and enamels can be successfully applied to the molded articles with no tendency to bleed or stain the painted surface. Various painted and lacquered samples exposed on the paint test fence for 2 years show that the plastic has paint-holding properties superior to either wood or metals.

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[3] E. C. Sherrard et al, U. S. Patents 2,216,866; 2,137,119.

These materials can be readily molded about relatively heavy metal inserts, as in a molded steering wheel, with no difficulty whatever and, we believe, in addition to being cheaper than the commonly used moldings, they have superior ageing characteristics and should be very suitable for such use as well as for gear shift knobs, and other articles where their black color is not objectionable.

In view of the present shortages of resins for molding compounds, it is very interesting to note that savings of up to 50 percent in resin content can be made by substituting hydrolyzed wood for the ordinary wood flour filler. That is, molding powders consisting of 25 to 30 percent phenolic resin with hydrolyzed wood, produce molding compounds comparable to general purpose powders containing 45 to 50 percent resin, with ordinary wood flour filler in respect to flow and strength (8,000 to 13,000 pounds per square inch flexural) and even superior water resistance (0.2 to 0.3 percent water absorption, 48-hour immersion).

Thus substitution of hydrolyzed wood for unhydrolyzed wood flour could be the means of increasing the amount of molding powder that can be produced from a given amount of phenolic resin by 60 to 100 percent with no sacrifice in quality or molding characteristics.

Pilot Plant

Numerous inquiries have been made as to cost of a plant for producing these molding powders. Since the work of the Laboratory has been on a small experimental scale, the next step would be a pilot or semi-commercial plant which could be expanded to commercial production.

Such a plant, capable of producing 2 tons of molding powder per day, would require the following equipment, or its equivalent:

Tumbling digester having a capacity of approximately 960 pounds of sawdust

Filter and washer having a capacity of one digester charge

Drier, rotary vacuum, 4'6" I.D. by 20'0" in length.

One equipment manufacturer has designed such a plant, capable of producing 2 tons per day of finished product by operating the digester and filter 10 hours per day and the rotary vacuum drier 24 hours per day. The daily production in the tumbling digester would be handled in six cycles of 100 minutes each, making a total of 10 hours. The daily production in the rotary vacuum drier would be handled in two cycles of 12 hours per day. It has been estimated such a plant would cost approximately $11,000.

Present Status

For the past few years three concerns have been very active on the commercial development of lignocellulose molding materials, in general consisting of modified lignocellulose produced from hardwood waste.

The Marathon Chemical Company of Rothschild, Wisconsin,[4] produce their materials either in the form of sheets suitable for laminating, or in the form of molding powders.

The Northwood Chemical Company of Phelps, Wisconsin,[5] produce a phenolic resin plasticized lignocellulose said to have excellent flow and curing characteristics.

The Burgess Cellulose Corporation of Freeport, Illinois,[6] have produced modified lignocellulose molding powders of both thermoplastic and thermosetting types.

As interest in this type of molding material is increasing at a rapid rate, and since any method of increasing the output of molding materials will have a great effect on both National Defense and civilian molding activities, it is anticipated that these materials will soon be on the market in ever increasing volume.

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[4] G. C. Howard. Lignin Plastics from Pulp Liquor Wastes. Modern Plastics 17(3):96 (1939).

[5] E. T. Olson and R. H. Plow. U. S. Patent No. 2,156,160.

[6] A. W. Schorger et al. U. S. Patents Nos. 2,247,204; 2,247,205; 2,247,206; 2,247,207; 2,247,208; 2,247,209; and 2,247,210.

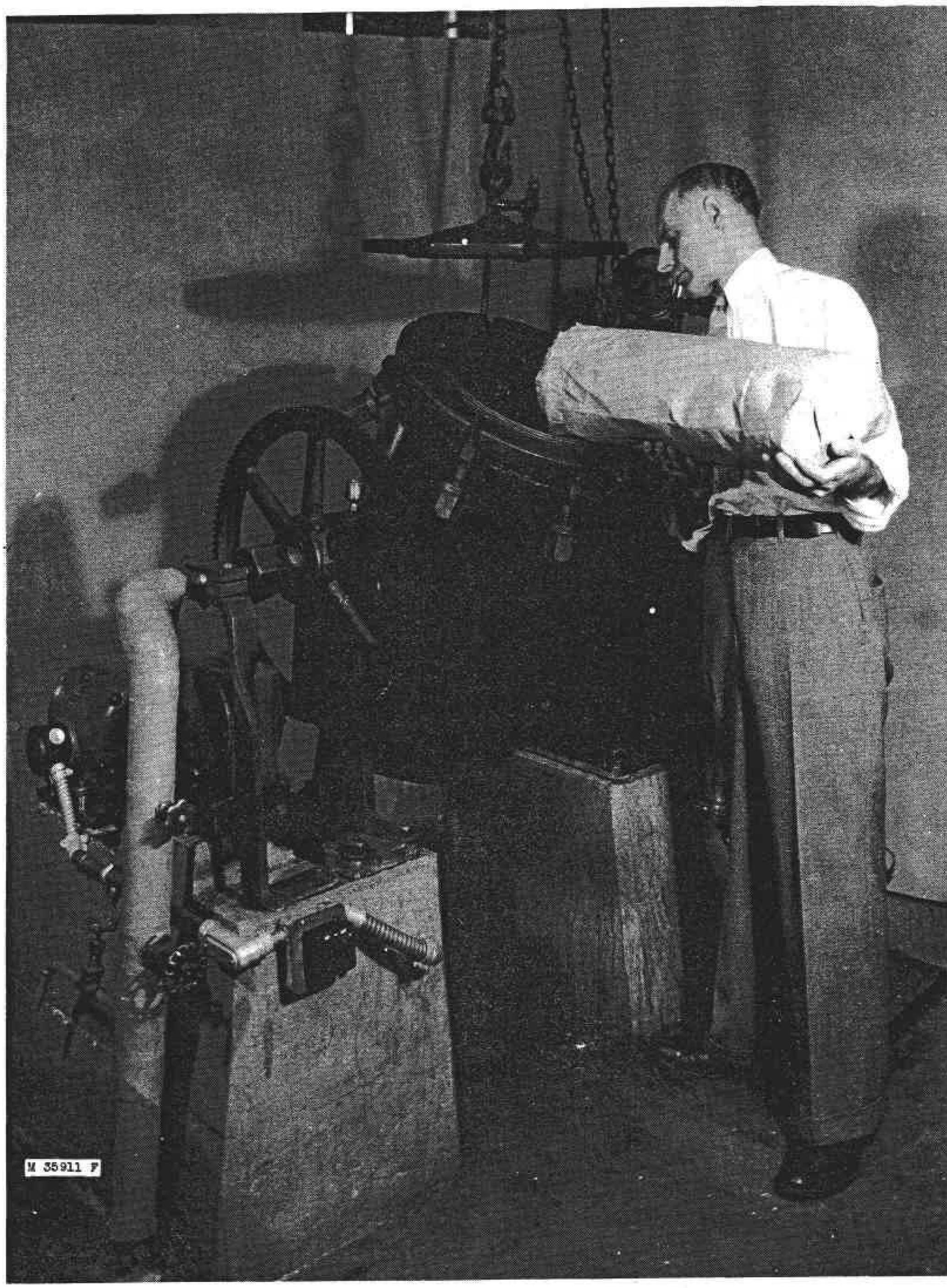

Figure 1.—Putting sawdust into an experimental digester for cooking.

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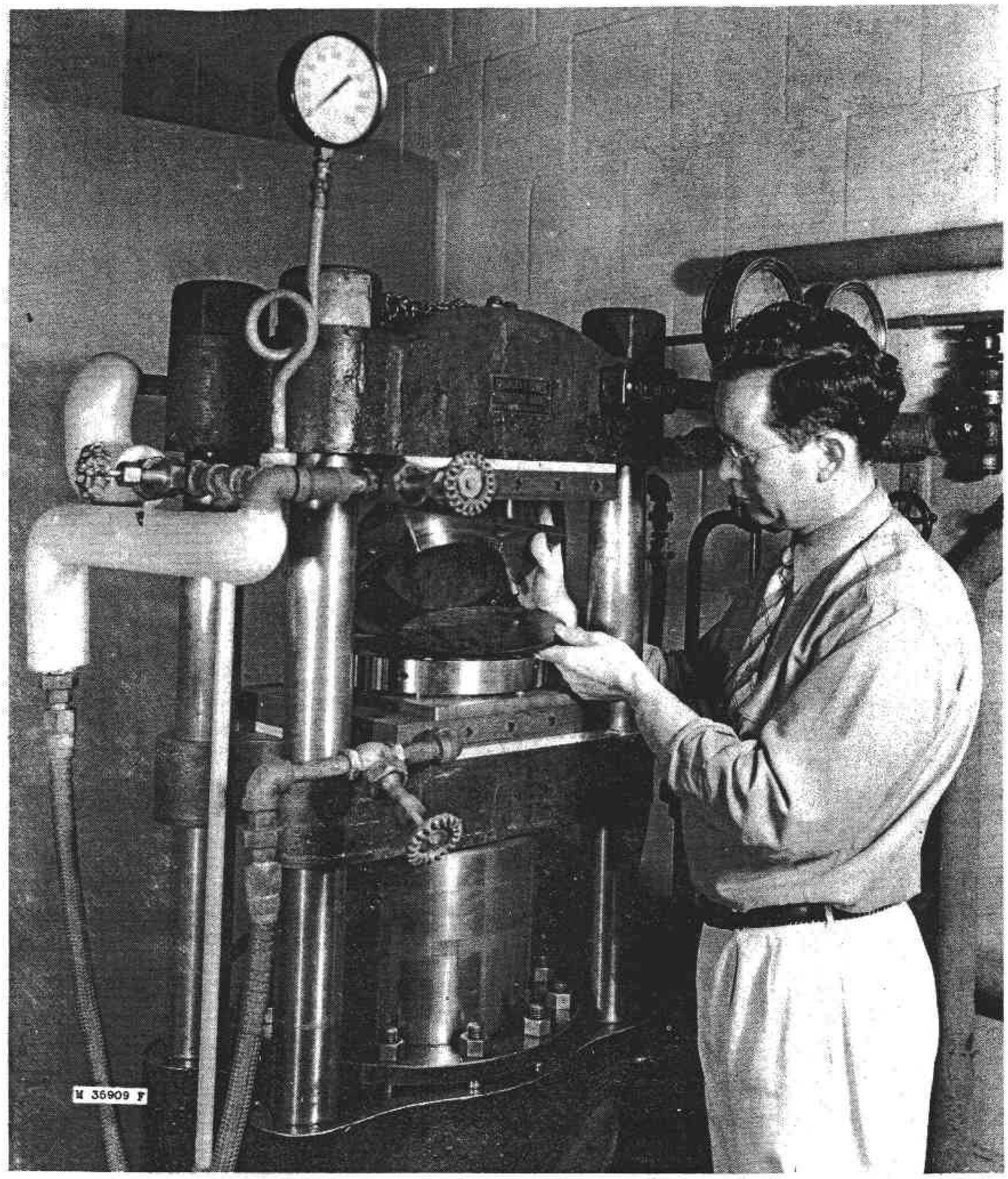

Figure 2.--Removing a disk of plastic from the highly polished mold after pressing. This specimen was finished with a thin overlay of fancy walnut veneer.

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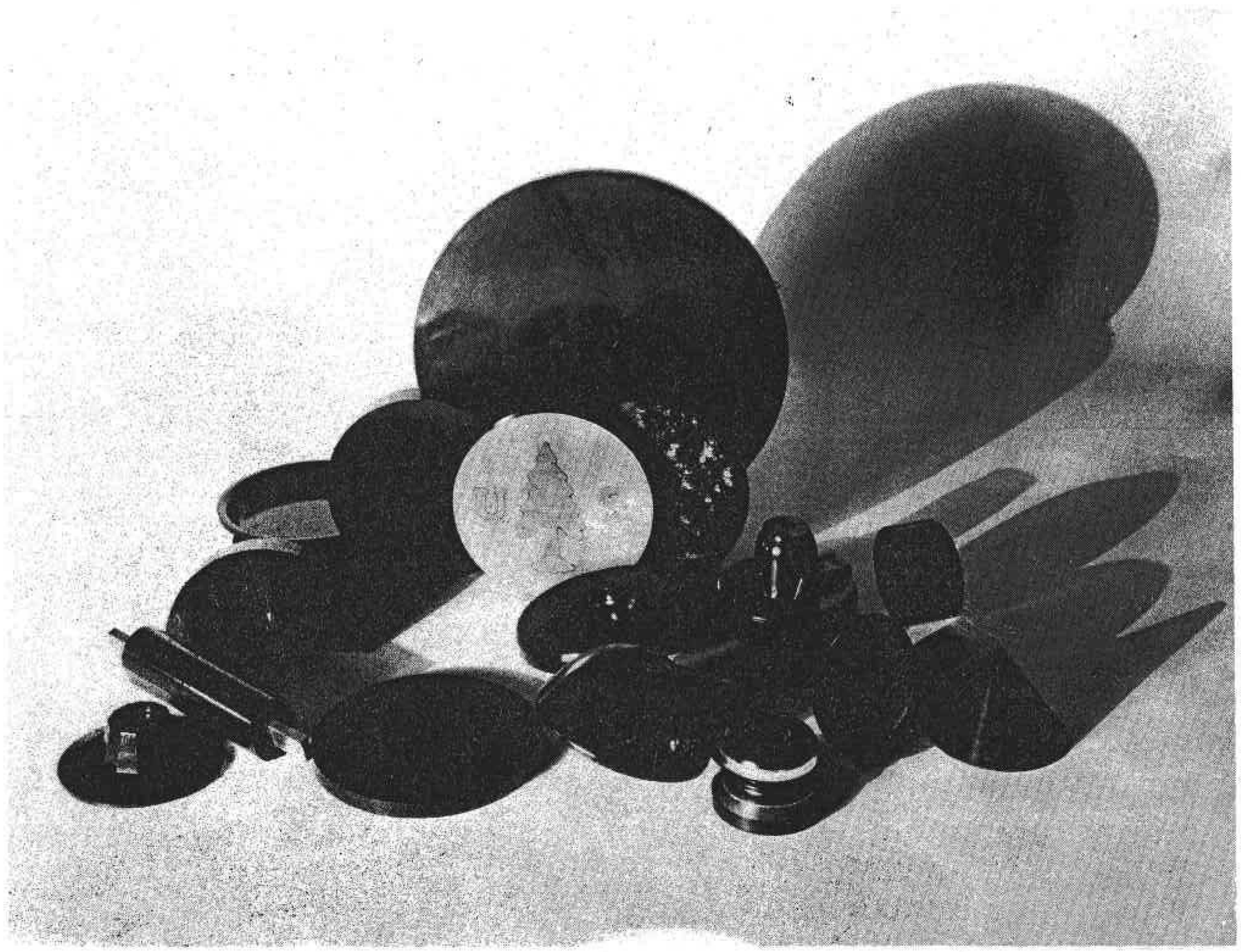

Figure 3.--General character of final material -- adaptable to many forms and products.

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