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DIGESTING LIGNOCELLULOSE WITH A ROSIN SOAP

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This invention relates to an improved ligno-cellulose material and to a process for its manufacture. More particularly this invention involves a method of treating ligno-cellulosic fibrous material which results in a product of improved properties when used for the production of sheet-like, as well as other shaped materials, by the use of heat and pressure.

It has been found that an improved molded product can be formed by the simultaneous pressing and heating of a sheet of ligno-cellulosic material, if the fibers so treated have been previously cooked in water under pressure. If the proper cooking procedure is followed, the strength and water resistance are greatly improved. While this method of treatment produces a substance, when formed by heat and pressure into a sheet, having properties which are an improvement over that formed from ligno-cellulosic material not so treated yet it has been found that the sheets so formed are brittle and that the yield is considerably reduced.

It has been found that the yield and brittleness can be improved if the cooking of the ligno-cellulose material is not carried to the point that substantially all of the hemicellulose is removed. This point appears to be when the yield on a bone dry basis is 70% or over. However, when this semi-cook is made, preferable to giving a bone dry yield between 80 to 90% the resistance to water penetration is considerably less than for a more complete cook such as will be shown by the lower yield. This can be overcome by adding a high percentage of a water proofing material in a manner which will be subsequently set forth.

The usual method of improving the water resistance of fibers is by the addition of rosin size or similar water proofing material to the pulp either in the beater or in the stuff chest followed by the addition of an acid generating material such as alum to effect the precipitation of the rosin soap upon the fibers. This method of water proofing is practical only to a limited extent in the production of hardboard. It can not be used to add the quantities needed to give the waterproofness needed for many purposes. By practicing this invention it is possible to attain a marked improvement in the water resistance as well as other characteristics of a heat and pressure consolidated product formed from cooked wood such as hardboard by a simplified and economical procedure.

Hardboard is a sheetlike commercial product

obtained by compressing fibers into a hard dense sheet by the use of heat with pressure, preferably to a density of between 40 to 75 lbs. per cu. ft. Its strength and water resistance resembles wood but it is much more uniform in properties than wood. Since the manufacture of hardboard is one of the outstanding purposes for which this invention can be used, it will be used in the forthcoming examples of means by which this invention may be carried out. Such use is only exemplary as other material which are not sheetlike in form can be made following this patent.

It is the purpose of this invention to disclose a heat and pressure consolidated product, especially hardboard, which has properties superior to those produced in the past, such, for example, as improved pressing characteristics, minimized efflorescenses, less tendency to disintegrate with age, much less brittleness and a relatively high strength and resistance to water absorption. While an improved product is formed by this invention, it is also an object of this invention to show means by which such a product can be obtained by a more economical and simplified method.

In the cooking of ligno-cellulosic material such as wood, particularly those known as hard wood, with water, there are formed acids which are discarded and generally are not used for any commercial purpose. It is one of the objects of this invention to utilize these acids in the waterproofing of the fibers by the precipitation of the waterproofing material from solution so that it becomes an integral part of the fibers simultaneously as the fibers are being cooked under pressure. It has been found that when the waterproofing material is added to the digester, such as with the water to be used for cooking, the acids formed during the decomposition of the woods causes it to precipitate whence it becomes associated with the fibers.

For the purpose of illustration and to describe a preferred embodiment of this invention, a waterproofing material is selected as an example which is commonly used in the art, and known as rosin size or substantially sodium abietate. However, it is not the intention to limit the scope of this invention thereby as other waterproofing materials which are precipitable by acids can be utilized. Examples of such materials are the sodium, potassium or ammonium soap of the saturated or unsaturated fatty acids as well as abietic acid or rosin. Rosin size is preferred because of its lower cost, effectiveness and its adaptability to the process.

In carrying out this invention it is preferred to use the cooking procedure disclosed in a copending patent application, Serial Number 461,388, now abandoned, the subject of a separate invention and filed jointly with another inventor.

The wood to be utilized for the purpose of this invention can be either hard or soft wood. or a mixture of the two. The wood—such for example as cottonwood or willow—is first debarked by any suitable means, or the bark can be left on if desired, and then comminuted such as into chips about the size used in the manufacture of chemically cooked wood pulp. An excellent size of chip for this purpose is one having dimensions of approximately one inch by two inch by one-quarter inch. These chips are charged into a suitable digester capable of withstanding the intended pressure. A completely enclosed vessel of the well known spherical type is excellent for this purpose. After the wood chips have been charged into the vessel or digester a sufficient amount of water is added to bring the ratio of wood chips to water about equal to two parts of water to one of dry wood. The desired quantity of rosin size can then be added. Five per cent on the basis of the bone dry wood will give good results though in many cases only one per cent is sufficient. The rosin size can be any commercial grade as commonly used in the trade; it may be found desirable, in order to facilitate complete intermixing of the rosin with the digesting liquor, to first add the rosin size to water before adding to the digester. The digester is then heated externally or by the addition of steam or both.

If desired a very high percentage of rosin size can be added to obtain further improvement in properties. This is entirely possible by this method; amounts as high as 12% or more can be added. If pulp is used, instead of chips, the ratio of water used should be increased such as to 5 parts of water and 1 part of bone dry pulp.

It may be found expedient from the commercial standpoint to heat rapidly to the desired temperature and pressure and then hold at this point for the required time. A slower method of heating is preferred, if possible, as it allows a greater penetration of the rosin size into the fibrous material before it is precipitated by acids generated by cooking. After the desired temperature has been reached for carrying on the cooking, the time required to complete the treatment is a function of the size of the chips as well as that of the pressure used.

When the cooking is carried out under steam pressure it is preferred to use temperatures rather than pressure, to control the heating operations as the presence of air or other gases, within the digester, may so influence the pressure that the temperature obtained is not that corresponding to saturated steam at the pressure indicated. Because of this, it is always desirable to release the digester before it has finally reached its temperature to remove the air or gases. The usual time to release the digester is at a temperature slightly over 212° F.

It has also been discovered that, besides entrapped air, there is also a decomposition of part of the wood into gases under certain conditions which may not permit saturated steam tables to be used for obtaining the true temperature from the indicated pressure. However, whenever the heating has proceeded to the point where an appreciable quantity of gases are generated, it has proceeded too far to give the most optimum all around results. Hence, it is desirable not to carry on the digesting operation any further than is necessary; and the formation of a generous quantity of gas is a sure sign that the operations have been carried too far and should be stopped immediately. One of the purposes of cooking the wood is to decompose the pentosans, or the non-lignin and the non-cellulosic elements, contained in the wood. The lignin and cellulose portion of the wood are its most valuable constituents and to destroy them would be defeating one of the objects of this invention.

A range of temperatures from 335° to 385° F. and time from one half to one and one-half hours have been found very satisfactory for chips of the size used in the paper industry, such as about one by two by one-quarter inches. Slight adjustments in the time and temperature conditions can readily be made in order to give the best pulp from the kind and size of natural ligno-cellulose material and digester used. For the size of chips referred to above and for willow, a cook of 45 min. at 340° F. is satisfactory. The higher the temperature used, the lower the time required for cooking, but in general it has been found that better results are obtained at the lower temperature.

When the chips are properly cooked they retain their shape and upon mild refining produce a pulp which is fibrous in nature rather than mushy. In other words, a relatively free pulp can be produced which is strong and easy to felt. It will be found that the chips cooked with rosin size as described above will be more fibrous and stronger than when not so cooked and still the yield is higher.

The wood should, therefore, only be cooked sufficiently to generate enough acid to precipitate the rosin size and to destroy a portion of the hemi-cellulose or non-lignin or cellulose material present in the wood. A "raw cook" is preferred. A measure of the proper cook can best be made by the yield of wood obtained after the cooking operation. If the yield is between 80 and 90%, based upon bone dry weights of the pulp alone, the most desirable results have been obtained. A yield as low as 70% is undesirable. It is one of the purposes of this invention to only cook sufficiently to obtain the desirable properties of a water cooked pulp with the minimum of the disadvantages. It has been found that substantially all of the desirable properties can be obtained by a "raw cook" that is one giving a yield of from substantially 80 to 90% based upon the bone dry pulp. The strength and water resistance are appreciably improved, while the yield is good and there is little trouble with brittleness. However, for many purposes it will be found that the water absorption of the finished product will be too high, and to lower this the addition of some sort of sizing material is necessary. As mentioned above, the usual method of improving the water resistance, such as by the addition of rosin size to the beater, has many disadvantages when applied to hardboard manufacture.

Some of these disadvantages are: Only a small quantity can be added because of difficulty in forming due to gumming up of the felts and forming equipment and to blisters and sticking during pressing when a large quantity of size is used. Also, there is a marked tendency for board formed from sheets sized in this manner to produce an efflorescence due to discoloring soluble salts appearing upon the surface of the sheet.

By following this invention and adding the material to improve the water resistance to the cooker before or during the operation, a marked improvement in water resistance is noticeable along with increased strength. Also, the yield is higher, and since very little sodium salts are present after washing very little efflorescence will be noticed. In addition, the fibers will be tougher and hence in a more desirable state to form a mat preparatory for pressing. Thus one of the essences of this invention is to form a tough, strong hardboard of high resistance to water absorption by lightly cooking a natural ligno-cellulose material simultaneously with the incorporation of a water repellent material therewith. The water repellent material is precipitated by the acid formed during cooking.

After the cooking period has elapsed, the boiler is then blown down and the liquor discarded or further used to recover by-products. The liquor is acidic and is dark in color. It is desirable to remove the cook liquor and then wash or leach the chips several times with water at about a temperature of between 100 to 150° F. This will remove the soluble salts and sugars. The sugars cause sticking in the press and the soluble salts cause efflorescence on the surface of the finished board later on.

The chips can be disintegrated into fibers by pulping with water in a suitable mill, such as an attrition mill of the rotary disc type. The fibers are much more easily pulped since the natural bond between the fibers have been loosened. The fibers themselves have not been appreciably changed, but will be found to be highly water resistant, part of which is due to the waterproofing action attained by the above described procedure.

The pulp can be washed and deckered if desired, after first removing oversized chips and dirt by screening, or the pulp can be run directly to the stuff chest. Water is added to bring the consistence of the pulp to between 3 to 4 per cent. Other materials can be added at this time to the pulp if desired, such as drying oils, dyes, fillers, etc.

It will be found that none of the above processing of the fibers will remove the rosin size which appears to be firmly adhered to the fibers in some unexplainable manner after precipitation. For some unknown reason the water resistance of the resultant heat and pressure formed product is considerably improved if the pH of the pulp is on the acid side such as approximately 4.8. Thus, it is desirable to add an acidic material such as sulphuric acid, alum or ferric sulphate to the stuff chest to bring the pH to 4.8. It will also be found that owing to the absence of a substantial quantity of alkaline salts, a much less quantity of acid will be needed.

The pulp is then diluted with water to a consistency of from one-half to one per cent of dry fiber, preferably with the pH still maintained at 4.8. This pulp is formed into a coherent sheet upon some type of board forming machine such as a rotary cylinder or a Fourdrinier. The thickness of the sheet is usually from one-half to one and one-half inches, depending upon the final thickness of the consolidated board to be made. However, it is within the scope of this invention to form a thin mat, and to use several layers, along with a suitable adhesive, to make a single sheetlike product. The extraneous moisture is removed from the sheet by first passing through suitable press rolls and then into a dryer in which the remaining moisture is removed by the use of heat. The dried sheet or mat is then transferred to a suitable press with platens by which the mat is consolidated with pressures from about 500 to about 2500 pounds per square inch, depending upon the density desired, and at a temperature range of from 350° to about 560° F. The pressing time at a lower range of temperature may be from ten to twelve minutes while near the upper range of temperature the pressing time may be only a few seconds. The following conditions have been found satisfactory in making strong sheetlike material known as hardboard from a dried mat prepared as described above: temperature 450° F., pressure 800 lbs. per square inch, time 2 minutes. Under these conditions a board having excellent dry and wet strength is produced using pulp prepared as described above. This hardboard will be found to be superior to one prepared from fibers made in the usual manner.

It is also within the scope of this invention to hot press the wet mat, using a wire screen with or without any appreciable drying such as disclosed in U. S. Patent No. 1,663,505 to form a hardboard type of material. In such case a lower temperature and pressure may be used, but an increase in time is necessary because of the amount of moisture to be removed. Obviously other methods of forming the fiber into a sheet, as well as other methods of pressing or consolidating the fibers into a hard substance, may be used and still be within the scope of this invention.

The hardboard after pressing is cooled and stored under conditions permitting it to normalize according to the moisture content of the air. If desired, it may be trimmed and sized before normalizing. It is then ready for sale and shipment.

The following table clearly illustrates the improved properties attained by cooking hardwood pulp with a waterproofing material such as rosin size:

Specimen No.	Amount of rosin size used	pH of White Water	Density, lbs. per cu. ft.	Water absorption per cent weight increase after soaking 24 hrs. 70° F.	Modulus of Rupture, lbs./sq. in.
1	None used	No acid added.	70.4	48.7	7,620
2	5% during cooking	Same	71.2	12.8	7,850
3	None used	5	71.3	20.7	7,435
4	5% during cooking	5	71.2	9.4	8,078
5	None used—12% added to the beater.	4.8	68.2	9.8	6,890
6	12% during cooking	4.5	68.9	9.1	7,710

The above were all prepared under similar conditions and are accurate comparative results. Considerable trouble was encountered with blisters and sticking with No. 5 and it was only with great difficulty that a suitable hardboard was obtained for testing purposes.

As shown above, the addition of the rosin size to the digester during the cooking of the pulp improves the water absorption. In addition to these, other advantages of great importance to the quality of the resultant product formed are obtained, one particularly being the formation of a tough non-brittle hardboard.

An outstanding advantage of this method of treating fibers used in manufacturing products formed by consolidating with heat and pressure is that no additional alum or acidic material is required to precipitate the water proofing material upon the fibers. The waterproofing material has already been precipitated upon the fibers in the digester by the acids formed during cooking. However, as pointed out previously, it is more advantageous from the water resistance standpoint to reacidify the pulp after washing and before the formation of the mat. However, if an acid is not used, the white water will not be acidic, a very desirable advantage from the operating standpoint. Also, the product formed by consolidating with heat and pressure is not substantially acid, so that its deterioration with age should be less. It is well known that fibrous sheets which are highly acidic deteriorate more rapidly with age than those which are substantially neutral. While the water resistance of a non-acid sheet will be considerably higher than wood not cooked with the waterproofing material, it still will not be as good as if it had been acidified, though in some cases the improvements in other properties may outbalance the lower water resistance.

Another outstanding advantage obtained by following the principles set forth in this invention is the elimination, or at least a very substantial reduction, of efflorescence upon the surface of the hardboard. Efflorescence is the migration of soluble salts to the surface of the fibrous sheets in such concentration that their appearance can be readily detected upon the surface. The white discoloration presents an unattractive appearance, and it is always desirable to prevent its formation, if possible. Certain atmospheric conditions, particularly those in hot humid climates, bring out this situation more markedly. Since under this invention the sizing takes place in the digester, most of the soluble alkali salts such as sodium sulfate which were formed during the sizing operation are removed by washing, hence there is very little of this material remaining to contribute to efflorescence. This is true even when the pulp is made acidic after washing out the digester liquor, for the acid can be such as not to contribute to the formation of soluble salts, such for example as the use of alum, ferric sulphate or sulphuric acid.

One outstanding property of hardboard made from ligno-cellulosic fibrous material, such as wood, cooked in accordance with the principles set forth in this example is its excellent bending and shaping properties. Bends can be made substantially free from cracks under conditions which would cause cracking as well as other difficulties in the bending of hardboard prepared in a manner not in accordance with this invention.

Besides the advantages of improvement in the properties of the hardboard and other products, produced following this invention, over those of the prior art, there are also marked process improvements some of which are enumerated below. For example, the addition of the waterproofing material to the cooker greatly facilitates the control and introduction of the material into the pulp, as the amount of size can be added more easily and can be accurately controlled. It is much more expedient to add the waterproofing material to a digester than it is to add it continuously to pulp as is now the practice.

A more important advantage is that by treating cooked fiber as disclosed in this invention, it is possible to use a much greater quantity of rosin size than if it was added after cooking, without danger of sticking or blistering during the pressing of the sheets. Also, a high percentage of such material added to the pulp after cooking and disintegrating results in a serious problem in the formation of the wet mat. Such difficulties as excessive foaming, gumming up of the felts and forming cylinders are encountered. Sheets containing as much as 12% rosin size have been formed, dried and pressed without difficulty by adding the size to the digester. With 12% of rosin size added after washing the felts and cylinders would become gummy and sticky, the sheets would be slow in forming and practically every sheet pressed would have blisters and stick in the press.

Other advantages not mentioned will readily occur to those skilled in the art of which this invention is a part. Likewise, numerous modifications and alterations can be made in this invention without departing from its essence. Various changes can also be made in the materials used, such as the use of soft woods instead of hardwoods. It is also possible to apply this invention to the preparation of pulp from straw, bagasse, and other fibrous materials containing ligno-cellulose.

It is not clear exactly what takes place when ligno-cellulosic materials are cooked with a waterproofing material such as rosin size. One theory is that there is a combination of the free acid with the ligno-cellulosic material in some manner, which enables it to stay adhered to the fibers in a way which will permit processing without the disadvantage usually experienced when the addition is made to the pulp after its preparation. A resinous product appears to be present as the properties of the fibrous material when subjected to heat and pressure appear to be altered in a manner to indicate the presence of such a material. The precipitated material is very difficult to separate from or identify with the fibers when cooked therewith, though tests have established its presence. While it is difficult to identify the waterproofing material, it can not be accounted for in any other manner than being in some way associated with the fibers and is not lost in the digester liquors.

By rosin it is meant any of the materials commonly classified as rosin or related to rosin, such for example as hydrogenated rosin, disproportionated rosin, polymerized rosin, heat treated rosin, rosin oil, rosin acids or any of the color grades of rosin as known in the art, or a mixture of these materials with other materials such as the fatty acids. Also, it is not the intention to limit this invention to a rosin type of material for obviously the principles of this invention can be advantageously applied to other types of waterproofing materials which can be applied in liquid form by saponifying or other means which will give a precipitation with the acids formed during cooking, such for example as the soluble soaps of saturated or unsaturated fatty acids, drying oils, etc. Throughout this application the term "size" is to be construed to mean any waterproofing material in saponified form which will be precipitated by an acid. In such cases it may be found more advantageous to apply the materials in emulsion form such as mentioned previously. It is not necessary that all of the available material be neutralized; only enough to enable introduction to the digester. It is within the scope of this invention to add the saponified or acid precipitable material to the digester at any time during the cooking operation, which will give the best results. The material can be added near the end of the cook if desired. It is also within the purpose of this invention to control the rate or time of precipitation by adding acid or alkaline material to the digester. If an alkaline material such for example as 1% of NaOH is added to the digester along with acid precipitated material, the acids formed during the cooking of the wood are partially neutralized and the precipitation is retarded thus permitting a greater penetration into the wood.

By way of summary this invention covers the preparation of an improved stronger and more fibrous pulp material suitable for the preparation of articles molded under heat and pressure particularly from fibrous mats, such as hardboard, by cooking ligno-cellulosic material with water along with a waterproofing material such as rosin in saponified or emulsified form in which the generation of an acid during cooking will cause a precipitation upon and into the fibers along with a possible reaction therewith, the exact nature of which is not clear. The product thus obtained has superior properties such as higher strength and water resistance, improved bending and shaping characteristics substantially no efflorescence along with certain operating advantages, such as permitting a higher percentage of treating material to be used without danger of sticking or blisters forming during pressing and enabling a mat containing a high percentage of sticky sizing material to be readily formed without any appreciable slowing up of formation because of foaming or gumming up of the felts or to a decrease in freeness. This pulp has the further advantage that if a pH of around 5 is desired it can be attained with a much lesser amount of acidic material and with very little danger of forming soluble sodium salts. Because of the greatly improved water resistance obtained in hardboard formed from pulp treated in accordance with this invention, the cooking need not be carried as far, thus increasing the yield and improving the toughness and strength of the fibers over the full and complete cook. Cooking operation which will give a yield of 80–90% is sufficient and preferred.

Having disclosed a practical embodiment of this invention and specific examples, theories and uses which are given to insure a clear understanding of the essence of this invention, it is not the intention to be limited thereby for obviously many variations may be made by those skilled in the art and still be within the scope of this invention which is only limited in extent by the forthcoming claims.

It is claimed:

1. The method of producing a sized heat and pressure consolidated ligno-cellulosic product having a substantial quantity of water soluble material removed therefrom and substantially free from efflorescent salts, consisting of digesting at a temperature of 335° F. to 385° F. for ½ to 1½ hours, a comminuted natural ligno-cellulosic material with about one to five parts by weight of water containing as the essential component .01 to .12 parts by weight, based upon the bone-dry ligno-cellulosic fiber, of an aqueous dispersed pyroligneous acid precipitable soap selected from the group consisting respectively of ammonium, sodium and potassium soaps of rosin acid until an acid pH is attained and until at least a portion of the hemi-cellulosic material has been removed from said natural ligno-cellulosic material and washing said cooked comminuted ligno-cellulosic material substantially free from cooking liquor, further disintegrating said fibers into a pulp, forming said pulp into a shape substantially similar to said desired product and consolidating said shape under heat and pressure into said product.

2. The process claimed in claim 1 in which said soap of a rosin acid is rosin size.

3. The method of forming an improved sized hardboard of high strength and water resistance and substantially free from efflorescence consisting of cooking with about one to five parts by weight of water at a temperature of 335° to 385° F. at ½ to 1½ hours, a comminuted natural ligno-cellulosic material, said water containing as the essential component .01 to .12 parts by weight, all parts based upon the bone-dry ligno-cellulosic fiber, of an aqueous suspension of an acid precipitable waterproofing material selected from the group consisting respectively of the alkali metal and ammonium soaps of rosin acid, for a sufficient length of time to obtain a bone-dry yield of from 80% to 90% and to precipitate said waterproofing material by autogenously generated pyroligneous acids, removing the liquor from said cooked ligno-cellulosic material, further disintegrating said cooked ligno-cellulosic material into pulp-like fibers, washing said fibers to remove substantially all the water soluble materials, forming said fibers into a sheet, drying said sheet and consolidating said sheet under heat and pressure.

4. The method of forming an improved hardboard of high strength and water resistance and improved bending and non-brittleness properties consisting of digesting at a temperature of 335° F. to 385° F. for ½ to 1½ hours disintegrated natural ligno-cellulosic material in an aqueous suspension of about one to five parts water containing as the essential component between .01 to .12 parts by weight, all parts based on bone-dry ligno-cellulosic material, of a waterproofing sizing material selected from the group consisting respectively of the alkali metal and ammonium soaps of a rosin to obtain a bone-dry yield of from 80% to 90% and to autogenously generate pyroligneous acids to precipitate said sizing material, removing a substantial portion of the spent cooking liquors, further disintegrating said cooked ligno-cellulosic material into a fiber, forming said fiber from an aqueous suspension into a wet lap and simultaneously heating and pressing said lap with a foraminous surface on at least one face, whereby the water contained therein escapes during said pressing operation, until said wet lap has dried.

5. The process claimed in claim 4 in which said waterproofing sizing material is rosin size.

6. The process of producing a hardboard type product having a density of substantially between

40 and 80 lbs. per cubic foot consisting of cooking a comminuted natural wood-like ligno-cellulosic material with between about one to five parts by weight of water containing as the essential component dispersed therein from substantially about .01 to substantially about .12 parts by weight of said natural wood-like ligno-cellulosic material, based on bone-dry conditions, of a sizing material selected from the group consisting respectively of the alkali metal and ammonium soaps of a rosin to give a yield substantially corresponding to that obtained when said comminuted natural wood-like ligno-cellulosic material is cooked for substantially 45 minutes at 345° F. under substantially saturated steam conditions, washing the liquors from said sized, cooked, comminuted natural wood-like ligno-cellulosic material, refining said cooked material to a fibrous form, washing said fibers with water to remove readily soluble substances, diluting said washed refined fibers with water, adjusting the pH of said washed pulp to an acid pH, forming said diluted pulp into a shape similar to the shape of said finished hardboard, drying said shape to substantially a bone-dry condition and then consolidating at a temperature substantially between 350 and 560° F. and at a pressure of substantially between 500 and 2500 pounds per square inch, and from substantially twenty minutes to ten seconds, the shorter time used with the higher temperature, to form said hardboard product.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,633,738	Fish	June 28, 1927
1,682,834	Dedrick	Sept. 4, 1928
1,786,462	Stryker	Dec. 30, 1930
1,873,056	Smith	Aug. 23, 1932
1,945,862	MacIntyre	Feb. 6, 1934
2,047,170	Asplund	July 14, 1936
2,056,810	Smyser	Oct. 6, 1936
2,247,204	Schorger	June 24, 1941
2,247,206	Schorger	June 24, 1941
2,292,389	Meiler	Aug. 11, 1942
2,292,390	Meiler	Aug. 11, 1942
2,317,394	Mason	Apr. 27, 1943
2,375,414	Heritage	May 8, 1945
2,402,160	Heritage	June 18, 1946

FOREIGN PATENTS

Number	Country	Date
82,438	Austria	Jan. 25, 1921
649,669	France	May 26, 1914
35,854	Germany	June 10, 1886
314,146	Germany	Aug. 30, 1919