Sept. 3, 1957 W. P. LAWRENCE ET AL 2,805,118

MULTISTAGE PROCESS BLEACHING OF ALKALINE-PROCESS WOOD PULPS INCLUDING AN ACID SOUR BETWEEN TWO TERMINAL ALKALINE HYPOCHLORITE STAGES

Filed Aug. 7, 1953

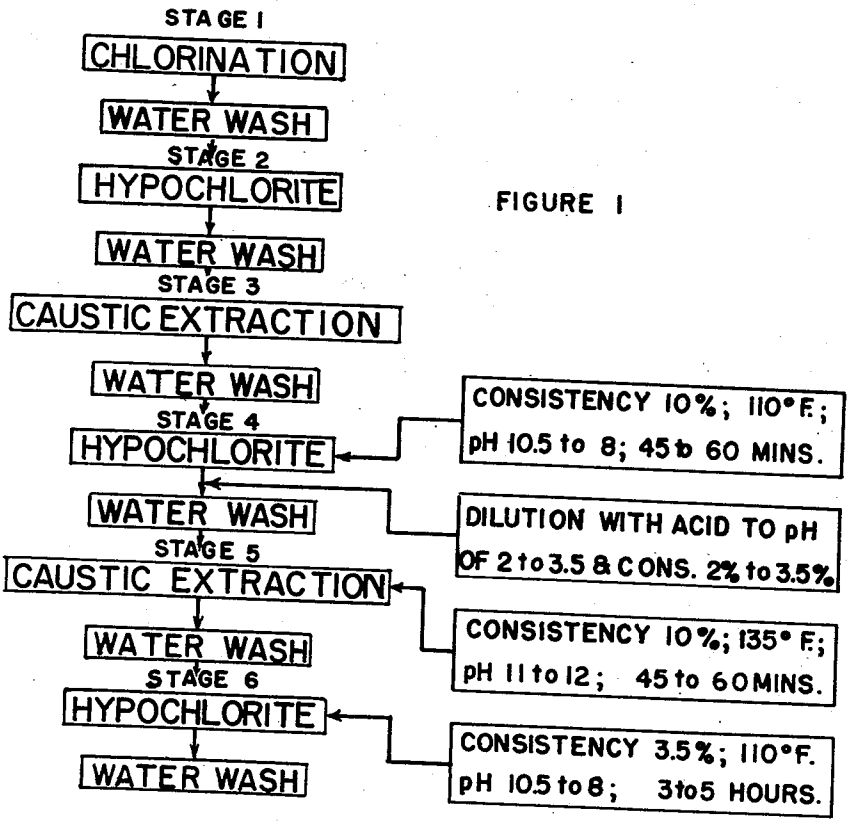


FIGURE 1

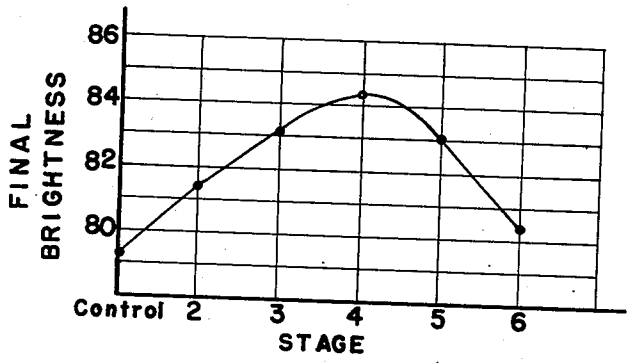


FIGURE 2

Walter Phalti Lawrence
Arthur C. Salisbury
Inventors

By John W. Teare

Attorney

United States Patent Office 2,805,118 Patented Sept. 3, 1957

2,805,118

MULTISTAGE PROCESS BLEACHING OF ALKALINE-PROCESS WOOD PULPS INCLUDING AN ACID SOUR BETWEEN TWO TERMINAL ALKALINE HYPOCHLORITE STAGES

Walter Phalti Lawrence and Arthur C. Salisbury, Hamilton, Ohio

Application August 7, 1953, Serial No. 372,936

8 Claims. (Cl. 8—105)

This invention relates to an improved multistage process for bleaching alkaline-process wood pulps, employing conventional chlorine bleaching agents, and specifically to a process having an acid treatment intercalated in a sequence of alkaline stages.

The difficulties in bleaching pulps to high brightness, that is to values of 75 and above, are well known in the art. The multistage bleaching process has done much in overcoming the difficulties; a reduction in the amount of available chlorine required, improved retention of pulp strength, and improved brightness has been secured with this process. A large amount of experimental effort continues to be devoted toward making the multistage process as effective as possible, by working out optimum conditions of temperature, amount and concentration of reagent, pulp consistency, time of contact, pH, etc.

In spite of the extensive effort put forth, and of improvements secured, the problem of suitably whitening pulp has not been answered completely. First of all, high brightness is still not easily obtained. Relatively large amounts of bleach are necessary, many extra steps are required (the number of stages being as high as eight or more in some cases), and in general large expenditures for equipment, power, and labor are necessary. In fact, with sulfate pulps a brightness barrier is encountered so that even ignoring precautions and expense it is a struggle to obtain 85 brightness.

Secondly, under the best conditions a high brightness pulp still is obtained only at a substantial sacrifice in pulp strength. While the loss in strength is not substantial in bleaching to a brightness of between 65 and 70, it becomes extensive when a brightness of 80 and above is developed. Apparently as the lignin and other color bodies are removed, the cellulose becomes more accessible and susceptible to oxidation and degradation. In bleaching alkaline-process pulps, especially sulfate pulps from coniferous woods, the degradation is more of a problem because of the inherent characteristics of the residual lignin which makes its removal much more troublesome. Consequently bleaching alkaline-process pulps to a brightness of 80 and above with good retention of fiber strength still constitutes a major obstacle. The last few points in brightness command a great premium in the industry.

One object of this invention is to provide an improved multistage process for bleaching alkaline-process wood pulps to a high brightness with improved retention of pulp strength.

Another object of this invention is to provide a process of bleaching alkaline-process pulps to a higher brightness for a given quantity of available chlorine applied.

Figure 1 is a flow diagram illustrating a preferred form of the invention. Figure 2 is a graph showing the relationship between brightness and point of modification of the bleaching process.

We have discovered that in a multistage bleaching of an alkaline-process pulp in which two alkaline hypochlorite steps are employed as the last two stages, a substantial increase in ultimate brightness is obtained if between the last two hypochlorite steps the pH of the pulp slurry is lowered to a value within the range of about 2 to 3.5 with a non-reducing acid. Thus, by intercalating an acid treatment between two final alkaline hypochlorite steps, in the particular manner described herein, a gain of from three to six points in brightness can be secured without any additional amount of available chlorine being applied, and without any material loss in pulp strength. The step of changing the pH from an alkaline to an acid value is designated herein as an "acid sour." In typical applications of our process the brightness may be increased from a value of 80 to that of 84, or from 82 to 86, with the pulp strength substantially the same at the high brightness as at the low. For example, a pine sulfate pulp when bleached by a conventional six-stage process had a brightness of 81.5 and a disperse-viscosity of 9.1, whereas when our acid sour, pH of 3.5, was applied after the fourth stage, the same pulp had a brightness of 85.1, and a disperse-viscosity of 9.7. In conventional operations raising the brightness, in this range of 80 and above, by 3.6 points would normally lower the disperse-viscosity substantially, not increase it. These benefits are singular in view of the susceptibility of the cellulose to degradation when purified to this extent.

The invention is dependent upon a combination of factors. Mere acidification of the pulp is not of itself enough. Some benefit is secured at most acid pH values. Similarly some benefit is obtained at several of the stages in the process. In general we have found that it is essential that the acid sour be applied after the next-to-the-last of two terminal alkaline hypochlorite stages. It is inconsequential what bleaching stages, and the number thereof, precede the terminal hypochlorite stages as long as they produce adequate preliminary bleaching.

Figure 2 illustrates the effect of an acid sour at different stages of a six-stage bleach. A pine sulfate pulp was divided into six portions and each portion was bleached under identical, conventional conditions by the steps of chlorination, hypochlorite, caustic extraction, hypochlorite, caustic extraction, and hypochlorite. A total of 8.5% available chlorine was applied to each portion. Portion one had no acid sour; in each other portion an acid sour, at a pH of about 2, was applied at the end of a given stage. The results shown in the graph clearly indicate the importance of applying the acid sour at the correct point in the sequence. With a six-stage process the acid sour should be applied at the end of stage 4, between the last two hypochlorites. In a four-stage bleach comprising chlorination, hypochlorite, caustic extraction, and hypochlorite, the maximum benefits are obtained with an acid sour at the end of the first hypochlorite. Similarly in a five-stage bleach consisting of chlorination, hypochlorite, caustic extraction, hypochlorite, and hypochlorite, the acid sour should be applied at the end of stage 4.

This maximum gain in brightness, however, is obtained only at a pH in the range of from about 2 to about 5.0. In a representative six-stage bleach the control (no acid sour) had a brightness of 80.6, while with an acid sour after stage 4 at pH 4.5, brightness was 82.4, and at pH 2.5, it was 84.1. Below a pH of 2 no further gain in brightness is secured. In some cases it is advantageous to carry out the acid sour at a pH as high at 3.5 since at this pH practically the optimum in brightness gain is secured, and the acid requirement and corrosiveness would be lower than at a pH of 2.

While the acid sour might be carried out as a separate step, it need not be. The next-to-the-last hypochlorite stage, for example, the fourth stage of the usual six-stage process, is conventionally carried out at a con-

sistency of about 10%. When the available chlorine of the next-to-the-last hypochlorite stage is substantially consumed, the pulp is diluted to about 2 or 3% in order to pass it over a rotary washer. In this dilution water we add acid in an amount sufficient to reduce the pH of the diluted pulp to between 2 and 3.5. Momentary holding of the stock at this pH appears adequate and no prolonged soaking is necessary. Substantially the same benefits are secured whether the stock is retained at this pH for 30 seconds, 3 minutes, or 1 hour. The consistency of the pulp in the acid sour operation does not appear to be critical; any consistency which facilitates handling of the stock at this point can be employed. Other methods of reducing the pH such as using acid water in the showers on the washer can be employed. Consequently, our procedure necessitates only the introduction of a suitable acid and adequate mixing. No extra handling of the stock is required, and no extra chests, filters, pumps, or other equipment is needed, except that required to introduce the acid.

The acid can be any of the commonly available non-reducing acids. We have used hydrochloric, sulfuric, nitric, and phosphoric acids interchangeably with essentially the same beneficial results. However, reducing acids have been found to give only a relatively slight increase in brightness. For example, a pine-sulfate pulp when bleached by a six-stage process similar to that of Figure 1, acidifying the stock during dilution after the fourth stage to a pH of 2, showed a 3-point increase in brightness (80 raised to 83) with hydrochloric acid, and only a 1-point increase (80 raised to 81) with sulfurous acid formed by the addition of sulfur dioxide. In the case of another pulp the normal six-stage bleach gave a brightness of 82.4, whereas when sulfur dioxide was introduced in the dilution water after the fourth stage to a pH of 2.4, the brightness dropped to 81.8, thus bringing about a loss. Similarly with oxalic acid employed in the acid sour after the fourth stage, only relatively small benefits in brightness are secured. The maximum benefit we have been able to obtain under any conditions with reducing acids has been 2 points, whereas with hydrochloric acid the gain has been as much as 6 points.

Contrary to what might be expected, we have found that the filtrate from a chlorination stage of this or a similar bleaching process can be used successfully to carry out our acid sour. In the usual multistage bleaching, from 40% to 70% of the total available chlorine to be employed is applied as chlorine in the first stage. The filtrate from such a stage contains not only hydrochloric acid but also a substantial amount of color bodies removed from the pulp. The reintroduction of such impurity-laden liquor at a later point in the process where the bleaching is substantially complete would not appear to be advisable. Yet, when we use such filtrate as the dilution liquor after the fourth stage, we have been able to gain as much as 5 points in brightness. In Example 1 which follows, we were able to obtain a brightness of 85 instead of 80 by this reintroduction of waste liquor from the first stage. Consequently, by our process, we are able to increase brightness materially with the use of the same chemicals, and with no increase in amount, with the same number of steps and amount of handling, and with no substantial loss in strength.

The improved process of our invention appears to be most effective when bleaching to a high brightness. While an increase in brightness can be obtained from our acid sour where the pulp is being bleached to 70 or 75, the increase is usually only one or two points. In bleaching to brightnesses above 75, and especially above 80, the increase obtained by virtue of the acid sour is substantial, of the order of three to six points, and of greater importance.

Our improvement can be used with practically all conventional multistage processes for bleaching sulfate, soda, and other alkaline-process pulps.

Figure 1 illustrates a six-stage bleaching operation representative of our invention. Stages 1, 2, and 3 as well as stages 4, 5, and 6, are conventional and need not be described in detail since procedure and conditions for multistage bleaching of alkaline process pulps are described in the literature. In general about 40% to 60% of the total available-chlorine is applied as chlorine in stage 1 with a resulting pH of about 2. The remainder of the required available-chlorine is supplied as calcium hypochlorite in stages 2, 4, and 6 with the largest portion being applied at stage 2 and the smallest portion at stage 6. The hypochlorite stages are buffered to maintain a pH of at least 8 and preferably 9 or above to prevent degradation of the cellulose.

Stages 1, 2, and 3 rather than comprising chlorination, hypochlorite, and caustic extraction can also be chlorination, caustic extraction, and chlorination, or other suitable combinations of stages, fewer or greater in number. So far as we have been able to determine, the beneficial effects of our acid sour are peculiar to a sequence of two final alkaline hypochlorite steps, either with or without an intervening caustic extraction stage. A final treatment with sulfur dioxide or other acid as is ordinarily applied, can be included.

Example 1

A pulp from pine wood chips cooked by the sulfate process was bleached by a conventional six-stage operation. Stage 1—the brown stock was chlorinated at a consistency of about 3% for 1 hour. A water wash followed. Stage 2—the stock was treated with calcium hypochlorite at 5% consistency for 1 hour. A water wash followed. Stage 3—the stock was extracted with caustic soda at 10% consistency for 1 hour. A water wash followed. Stage 4—the stock was treated with 1% available chlorine (basis oven dry pulp) as calcium hypochlorite and held for 1 hour at 10% consistency, and 105° F., the pH ranging from 11.2 to 10.4. It was then diluted to 2.5% consistency and water washed. Stage 5—the pulp was extracted by applying 1% of caustic soda on the pulp and holding for 1 hour at 10% consistency, 150° F. and a pH of about 11. A water wash followed. Stage 6—about 0.5% of available chlorine (basis oven dry pulp, as calcium hypochlorite was applied and the pulp held for 5 hours at 5% consistency, 110° F., and a pH ranging from 10.4 to 8.5. A water wash followed. Brightness of the pulp was 80.5, and the disperse-viscosity was 10.2 centipoises.

A portion of this pulp was taken after the expiration of the one-hour hypochlorite treatment in stage 4. Instead of being washed in the usual manner, filtrate from stage 1 was added in sufficient amount to reduce the pH of the stock to 3.5 during the dilution. Consistency of the stock to the washer was 2.5% in both portions. After the washer this second portion was processed through stages 5 and 6 in identical manner as the first portion. Brightness of the pulp was 85.7 and the disperse-viscosity was 9.9 centipoises.

Example 2

A sulfate pine wood pulp having a permanganate number of 16.2 was bleached in the following manner. The pulp was treated under conventional conditions with chlorine, then hypochlorite, and extracted with caustic soda, with a water wash after each of these stages. At this point the stock was divided into several portions. The first portion was treated (stage 4) with calcium hypochlorite (0.45% available chlorine, basis oven dry pulp) for 1 hour at 10% consistency, pH of about 9, and 105° F. It was then diluted to 2.5% consistency and washed on a rotary washer. The final application of calcium hypochlorite (stage 5) was made at 0.30% available chlorine, basis oven dry pulp, for 5 hours at 5% consistency, pH of about 9, and 110° F. A final water wash was then given the pulp.

In this case there was no caustic extraction between the two hypochlorite steps used to complete the bleaching. Brightness was 80.3 and disperse-viscosity 10.0 centipoises.

With the second portion treatment was identical with the first, except that after stage 4, in diluting the 10% consistency stock down to 2.5% for washing, hydrochloric acid was added in sufficient amount to lower the pH of the stock to 3.5. The brightness of the pulp was 83.6 and its disperse-viscosity was 10.0 centipoises.

The third portion was treated in identical manner as the first portion except that a caustic extraction was inserted between the two hypochlorite treatments, stages 4 and 5. It was carried out with 1% sodium hydroxide basis oven dry pulp, at 10% consistency for 1 hour at 150° F. and a pH of about 11. A water wash followed. Brightness of this pulp was 81.5 and its disperse-viscosity was 9.1 centipoises.

These results point out the benefit to be derived from an acid sour between the last two hypochlorite stages. Portion one and portion three differed only in that a caustic extraction was used in three. Comparing brightness this extra step gave an increase of 1.2 points (80.3 as against 81.5). Comparing portions one and two, shows that the brightness was increased by the acid sour from 80.3 to 83.6, an improvement of 3.3 points. It can be seen that at least in some instances the pulp is benefited by our invention as much or more than the caustic extraction, which is a complete extra stage.

Example 3

A sulfate pine wood pulp was bleached by a six-stage process in which the first three stages were chlorination, caustic extraction, and chlorination, with a water wash following each stage.

Stage 4 consisted in treating the pulp with calcium hypochlorite (3.5% available chlorine, basis oven dry pulp) for 75 minutes at 10% consistency, a pH of about 11, and 110° F. The pulp was then diluted to 2.5% consistency and washed. Stage 5 consisted in treating the pulp with caustic soda (1% basis oven dry pulp) for 1 hour at 10% consistency, pH of about 11, and 150° F. A water wash followed. Stage 6 consisted in treating the pulp with calcium hypochlorite (1.00% available chlorine on the oven dry pulp) for 5 hours at 5% consistency, pH of 8 to 9, and 110° F. It was then water washed. Brightness was 81.8 and disperse-viscosity 6.3 centipoises.

A second portion bleached in identical manner except that hydrochloric acid was added in the dilution at the end of stage 4 in amount sufficient to lower the pH to 3.5, and in stage 6 the amount of available chlorine applied was 0.50%. Its brightness was 84.8 and its disperse-viscosity 6.9 centipoises.

Example 4

A pulp produced from a mixture of hardwoods (red oak, red gum, and tulip poplar) by an alkaline process and having a permanganate number of 9.8 was bleached in four stages. Stage 1 was a conventional chlorination and was followed by a water wash. Stage 2 consisted of calcium hypochlorite (2% available-chlorine on the pulp, oven dry basis) treatment for 1 hour at 10% consistency, 95° F. and a pH initially of 10.6. A water wash followed. Stage 3 consisted of a caustic soda extraction with 2% NaOH on the pulp oven dry basis, for 1 hour, at 10% consistency, 135° F., and a pH of about 11. A water wash followed. Stage 4 consisted of a calcium hypochlorite treatment (1.50% available chlorine on the pulp, oven dry basis) for 3 hours at 3.5% consistency, 135° F., and a pH of 10.5 to 9.6. A water wash followed. Brightness of the pulp was 83.7.

A second portion of the same pulp was bleached under identical conditions except that at the eend of stage 2, hydrochloric acid was added to reduce the pH to a value of 2 during the dilution, preparatory to washing. The brightness of the pulp was 85.7.

The gain in brightness in this instance was not as large as in other cases. However, our procedure does apply to hardwoods as well as the more difficult bleaching softwoods. As in the other cases, an inversion of pH to the particular acid value, between the alkaline steps which are used to complete the bleaching, produces a definite increase in brightness. In fact, without our acid sour we have found it practically impossible to secure an 85 brightness hardwood alkaline-process pulp without excessive bleach or extra stages.

Our invention can be employed not only to obtain a higher brightness for a given amount of available chlorine applied, but to obtain a given brightness with a smaller amount of applied bleach. A pine sulfate pulp was divided into portions and each portion bleached by means of the six-stage process shown in Figure 1. Portion one was treated with 7.6% total available chlorine and no acid sour; its brightness was 81.9 and its disperse-viscosity was 12.7 centipoises. Portion two was bleached by the same procedure, differing only in that a total of 6.4% available chlorine was applied on the pulp (instead of the 7.6%) and an acid sour was applied at the end of stage 4 by reducing the pH of the pulp from a value of 9.0 to 3.5 by addition of commercial hydrochloric acid in the dilution water. Portion two had a brightness of 81.8 and a disperse-viscosity of 14.5 centipoises. Thus, the same brightness was obtained with about 15% reduction in the amount of bleach and with improved retention of strength.

The essential features comprise reducing the pH, at the end of the next-to-the-last hypochlorite stage of a multistage process, to a value between 2.0 and 3.5, with a non-reducing acid, where both terminal hypochlorite stages, and any caustic extraction stage intervening, are maintained at a pH of 8 and above. Our improvement has particular virtue in bleaching sulfate, soda, and other alkaline-process pulps.

Although sodium hydroxide is conventionally used for any caustic extraction between applications of bleaching agent, other alkali-metal hydroxides can also be employed for this purpose.

While the examples were all carried out with calcium hypochlorite, the other hypochlorite salts such as sodium, potassium and lithium can also be used.

The brightness readings given herein are those obtained by a General Electric brightness meter. Disperse-viscosities of the cellulose recited herein were determined according to Tappi Standard, T 230 SM–50, Cuprietylenediamine Disperse Viscosity of Pulp.

The term "alkaline-process woodpulp" refers to a pulp produced from wood by an alkaline digestion at an elevated temperature and includes sulfate, soda, and alkaline sulfite pulps.

We claim:

1. The method of bleaching alkaline-process wood pulp which comprises subjecting wood pulp which has been digested with an alkaline digesting agent at an elevated temperature to adequate partial bleaching in preliminary bleaching stages during which the major portion of the total bleaching agent used in the bleaching process is added to the pulp, said partial bleaching including at least a chlorination step, and completing the bleaching by the steps which comprise bleaching the pulp with an alkaline hypochlorite solution, subjecting the pulp after its bleaching with the alkaline hypochlorite solution and after the hypochlorite has been substantially all consumed during such bleaching treatment and the pulp is substantially free of bleaching agent to treatments involving reducing the pH of the resultant pulp slurry to between about 2.0 and 5.0 with an acidic material selected from the group consisting of non-reducing mineral acids and the filtrate from a previous chlorination bleaching stage and washing the pulp with water, and thereafter bleaching the pulp

with an alkaline hypochlorite solution, the pH and the duration of the bleaching steps being such as to impart to the pulp a brightness in excess of 75 General Electric brightness meter reading.

2. The process of bleaching alkaline-process wood pulp as set forth in claim 1 in which the pH of the pulp slurry is reduced to between about 2 and 3.5.

3. The process of bleaching alkaline-process wood pulp as set forth in claim 1 in which the pulp, after the slurry thereof has had its pH reduced and has been washed, and before it is given its final bleaching treatment with the alkaline hypochlorite, is extracted with an alkali-metal hydroxide and washed with water.

4. The process of bleaching alkaline-process wood pulp as set forth in claim 1 in which the pH is lowered to a value of between 2.0 and 3.5 by the additional filtrate from a prior chlorination bleaching step.

5. The process of bleaching alkaline-process wood pulp as set forth in claim 1 in which the pH is lowered to a value of between 2 and 3.5 by the addition of a non-reducing mineral acid.

6. The process of bleaching alkaline-process wood pulp which has been digested with an alkaline digesting agent at an elevated temperature to adequate partial bleaching in preliminary stages including bleaching an aqueous pulp slurry with chlorine, washing said pulp with water, bleaching said pulp with an alkaline hypochlorite solution, washing said pulp with water, extracting said pulp with caustic soda and washing said pulp with water, and completing the bleaching by the steps which comprise bleaching said pulp with an alkaline hypochloride solution, subjecting

the pulp after its last said bleaching with alkaline hypochlorite solution and after the hypochlorite has been substantially all consumed during such bleaching treatment and the pulp is substantially free of bleaching agent to treatments involving reducing the pH of the resultant pulp slurry to between 2.0 and 5.0 with an acidic material selected from the group consisting of nonreducing mineral acids and the filtrate from a previous chlorination bleaching stage and washing the pulp with water, and thereafter bleaching the pulp with an alkaline hypochlorite solution, the pH and the duration of the bleaching steps being such as to impart to the pulp a brightness in excess of 75 General Electric brightness meter reading.

7. The process of bleaching alkaline-process wood pulp as set forth in claim 6 in which the pH is lowered to a value of between 2 and 3.5.

8. The process of bleaching alkaline-process wood pulp as set forth in claim 6 in which the pulp, after the slurry has had its pH reduced and has been washed and before it is given its final bleaching treatment with the alkaline hypochlorite, is extracted with an alkali-metal hydroxide and washed with water.

References Cited in the file of this patent

UNITED STATES PATENTS

1,705,897	Bradley	Mar. 19, 1929
1,968,223	Rosen	July 31, 1934
2,178,649	Schuber	Nov. 7, 1939
2,186,487	Joachim	Jan. 9, 1940
2,203,205	Rawling	June 4, 1940
2,424,797	Casciani	July 29, 1947