

May 15, 1951

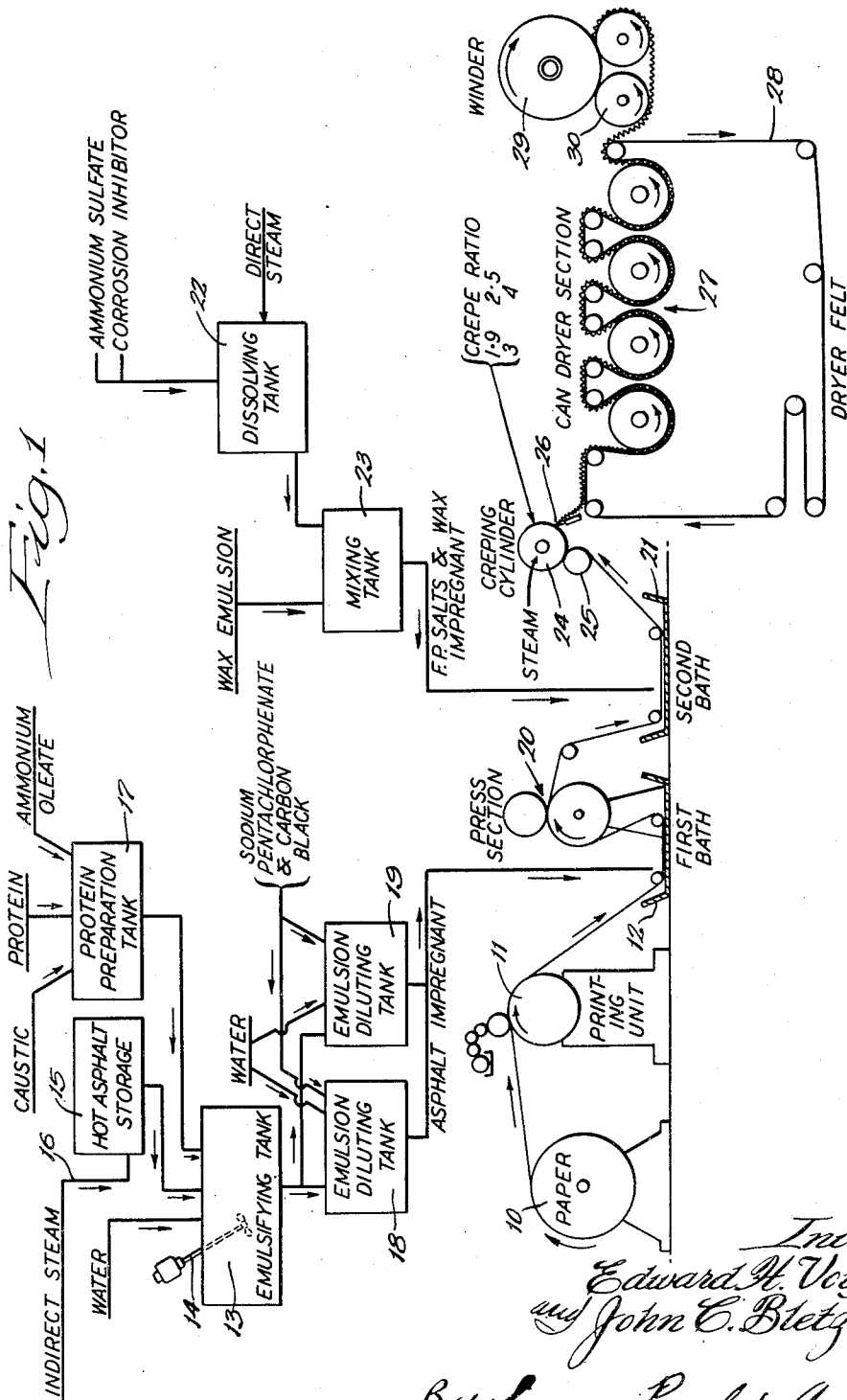
E. H. VOIGTMAN ET AL

2,553,154

METHOD OF WATERPROOFING AND FLAMEPROOFING PAPER

Filed Oct. 3, 1945

2 Sheets-Sheet 1



*Inventors.*  
*Edward H. Voigtman*  
*and John C. Bletzinger.*

*By Soans, Pond & Anderson,*  
*Attorneys.*

May 15, 1951

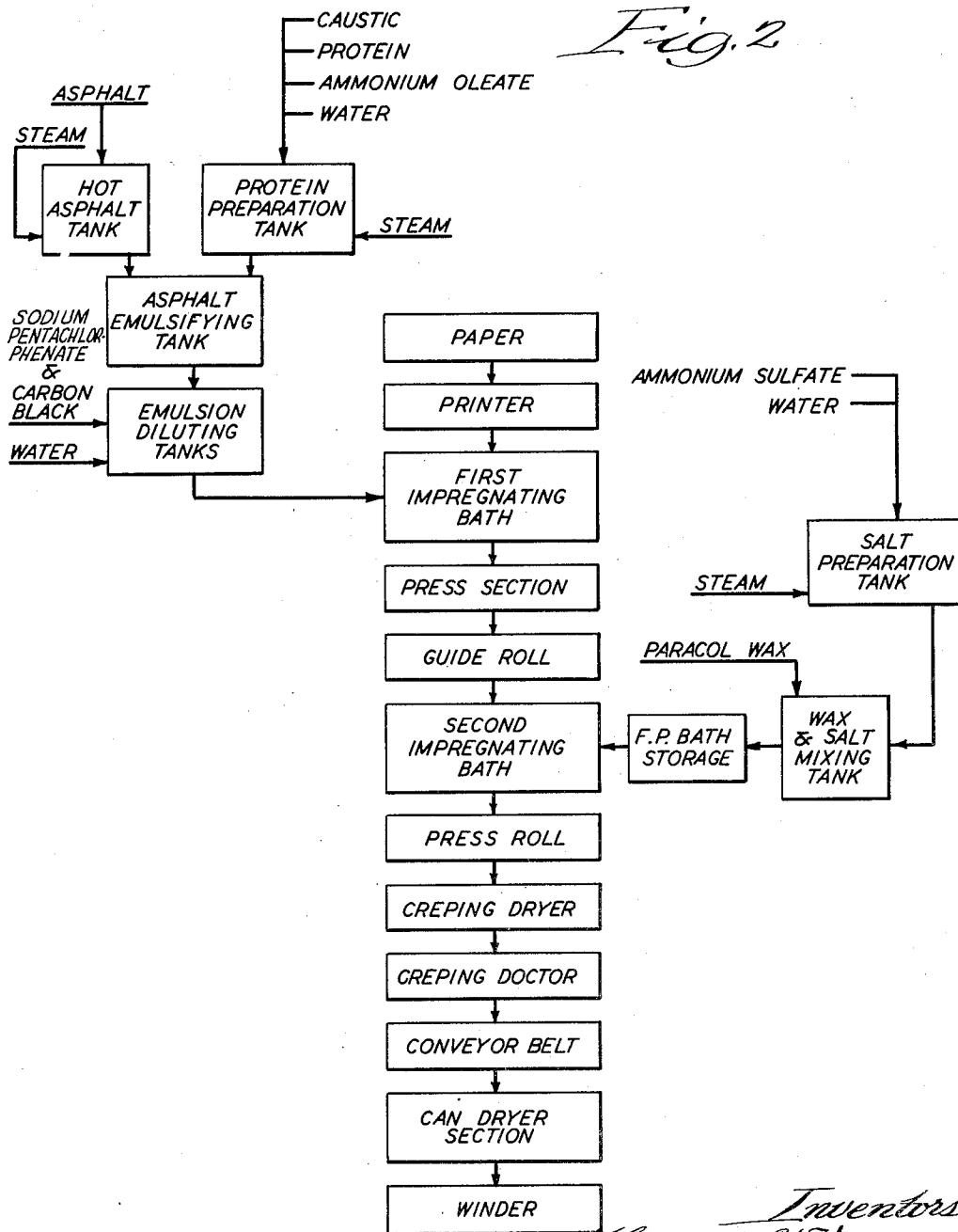
E. H. VOIGTMAN ET AL

2,553,154

METHOD OF WATERPROOFING AND FLAMEPROOFING PAPER

Filed Oct. 3, 1945

2 Sheets-Sheet 2



*Inventors:*  
*Edward H. Voigtman*  
*and John C. Bletzinger,*

*By Soans, Pond & Anderson,*  
*Attorneys.*

## UNITED STATES PATENT OFFICE

2,553,154

METHOD OF WATERPROOFING AND  
FLAMEPROOFING PAPER

Edward Hugo Voigtman and John Calvin Blet-  
zinger, Neenah, Wis., assignors to Paper Pat-  
ents Company, Neenah, Wis., a corporation of  
Wisconsin

Application October 3, 1945, Serial No. 619,976

5 Claims. (Cl. 117-137)

1

2

The invention relates to industrial paper and process of making same and relates particularly to the manufacture of a type of paper which may be used for various industrial purposes, for example as a facing sheet for blanket insulation, or for any other purpose where there is need for a paper which is relatively strong and flexible and which, at the same time, has substantial water-resistant and flame inhibiting or fire-resistant properties. For example, a sheet of the general character herein referred to can be employed to great advantage as the top or carrier sheet for a compressed bat of asphaltic multiply cellulose tissue crepe wadding insulation such as is disclosed in the Furness et al. Patents Nos. 2,339,326 and 2,341,370, or in the Randall Patent No. 2,254,856.

The manufacture of a sheet having the desirable properties of adequate water resistance, a reasonable degree of plasticity or flexibility, adequate mechanical strength while at the same time possessing such flame inhibiting or fire resistant properties as to reduce, or, at any rate, not to increase, the fire hazard of the structure to which the sheet is applied has heretofore presented great difficulties. The principal difficulty is due to the fact that asphaltum, the most generally used water-resistant substance because of its cheapness and other useful properties and advantages, is not compatible with those fireproofing substances which are commercially available by reason of cost or otherwise. It is understood that when herein we speak of two substances which are compatible, we mean that, when the fireproofing substance is dissolved in an aqueous solution, said aqueous solution can be used as the continuous phase of an emulsion in which the other substance, for example wax, exists as the discontinuous phase.

Similarly, a material emulsifiable in water may be said to be incompatible with a fireproofing salt which is usually a strong electrolyte, when a high concentration of the salt renders the emulsion unstable and causes the water-resistant material, which is the discontinuous phase, to be precipitated.

An asphaltum emulsion is incompatible in respect of strong electrolytes and therefore, when a sufficient amount of fireproofing salt to give the desired fire-inhibiting properties to an inflammable material such as paper is dissolved in the emulsion, the emulsion breaks or is rendered very unstable and cannot be used to the best advantage in treating the sheet for the purpose of imparting to the sheet those properties

which the asphalt treatment is intended to supply.

For the above stated and other reasons, the best results cannot be obtained by the use of a combined asphalt emulsion and aqueous solution of a fireproofing salt. Also for other reasons, it is not commercially practicable or desirable to employ a two-step process which involves the use of first an asphaltic emulsion and second a fireproof salt solution, or those steps in reverse order.

If the sheet is first treated with asphalt and then impregnated with a salt solution, the salt will be on the outside of the asphalt particles, and the water-resistant properties of the sheet will be, to a certain extent, impaired. On the other hand, it is desirable to impregnate with the fireproofing salt in the second step of the process on account of the fact that, in this manner, the fire-resistant or flame inhibiting properties of the sheet are superior to those of a sheet in which the asphalt treatment constitutes the second step of the process.

Hence, it is seen that the production of a highly water resistant and highly flame inhibiting sheet of the character described would seem to be practically impossible, because of the contradictory requirements. To obtain proper water resisting properties, the asphalt should be applied last. On the other hand, in order to obtain proper flame inhibiting properties, the fireproofing salt should be applied last.

Thus the purpose of the present invention is to reconcile the aforesaid contradictory requirements in the manufacture of a sheet which will possess in a satisfactory degree all of the desirable properties above mentioned and to enable such sheet to be manufactured at a reasonable cost by the use of conventional facilities.

*General method*

In general, our improved method of manufacture comprises, first, the manufacture of a strong bibulous paper sheet having incorporated within the body of the sheet a sufficient amount of asphalt or asphalt-like material in the form of an aqueous emulsion, to impart to the sheet the desired plasticity coupled with other desired mechanical properties, while at the same time of and by itself providing a substantial amount of water resistance. This asphalt loaded sheet, if necessary, is de-watered, or rather any excess emulsion is removed. Then the sheet is impregnated with a solution of fireproofing salt in which there is dispersed in the form of an emul-

sion a wax or wax-like substance, which, in the form of an emulsion, is stable to high concentrations of a strong electrolyte such as the flameproofing salt in solution. The sheet is then de-watered and dried. Before complete drying is effected, it is desirable to crepe the sheet, in the event that a creped final product is needed.

On account of the fact that waxes, which, in emulsion form, are compatible with strong electrolytes, are more expensive than common waterproofing materials such as asphalt, it is of course desirable to use no more wax than is necessary to augment sufficiently the waterproofing properties furnished by the asphalt. On the other hand, waxes of a suitable character are more efficient as water-repellent agents than asphaltum, and hence it is not necessary to use as large a percentage of wax as asphalt. Also, the amount of wax used should not be enough to reduce materially the flame-inhibiting properties supplied by the salt impregnation.

Various types of suitable waxes may be purchased. Any efficient water-resistant wax which can be emulsified to be stable in the presence of a strong electrolyte may be employed. We have had excellent results with wax emulsions which are colloidal dispersions of petroleum wax in an aqueous medium, stabilized and emulsified by a small amount of water-soluble gum and a water-soluble salt of an organic sulphonic acid. A similar emulsion of petrolatum may also be employed.

In certain cases the wax, or part of it, may be incorporated in the first bath which contains the asphaltum ingredient.

The finished dried sheet may contain from 4 to 18% by weight (based upon the weight of the finished sheet) of asphalt, from 9 to 16% by weight of a flame retardant such as ammonium sulphate and/or ammonium phosphate, and from 1 to 6% by weight of compatible wax.

#### *Specific example*

In the manufacture of industrial paper of the character described, for use as the outer cover or face sheet of an insulating blanket made of crepe wadding, we have obtained excellent results in the use of an apparatus and process such as are illustrated somewhat diagrammatically in the accompanying drawings. In the drawings:

Fig. 1 is a diagrammatic representation of the apparatus employed in the process; and

Fig. 2 is a flow sheet for said process.

Referring to the drawings, 10 represents a roll of raw or untreated paper such as unbleached kraft, in the present instance having a basis weight of 26 lbs. per ream of 3,000 sq. ft. This paper should be sized or otherwise treated so that it will retain enough mechanical strength to be fed through the impregnating baths without undue breakage, while at the same time the sheet should be in such condition as to take up the proper amount of emulsions or solutions in the impregnating baths.

If the finished paper is to bear any words or other markings, the sheet may be printed before it is subjected to the waterproofing and flameproofing treatment. Such printing can be effected in any appropriate type of web fed press, such a press being indicated at 11 in the drawings. From the printing press 11, the paper is directed into a first impregnating bath 12, which contains a water asphalt emulsion. Said emulsion is produced in the following manner.

The emulsification is effected in a tank 13

which is equipped with a high speed mixer 14. The asphalt which, in this instance, may be of a saturating type, is liquefied in a tank 15 heated by indirect steam through a supply line 16. The stabilizer for said emulsion is prepared in a tank 17 into which there are introduced separate supplies of caustic, protein, and ammonium oleate.

The protein used may be about eighteen parts soy bean alpha protein which is first suspended in about 4 times its weight of water, allowed to swell for one-half hour, and then heated to about 140° F. 2 parts by weight of 50% caustic soda solution are then stirred in, and the temperature is raised to 160° F., after which 9 parts by weight of ammonium oleate are added and stirred. Meanwhile, 72 parts by weight of the asphalt have been heated to 160° F. to form the emulsion. Enough of the prepared protein mixture is used to supply 1 part by weight of protein for each 4 parts by weight of hot asphalt, and sufficient water is added to the emulsifying tank to bring the total solids to about 30 to 32% by weight.

In making the emulsion, it is desirable first to add the protein mixture to the emulsifying tank. Then, while vigorously agitating the protein, the hot asphalt is added slowly. After the protein and asphalt have been thoroughly incorporated each with the other, enough additional water, at the same temperature, 160° F., is added to bring the total solids to the required 30 to 32% by weight.

Another type of stabilizer that has been successfully used is one which employs a thermoplastic resin derived from pinewood and containing phenol, aldehyde, and ether groups. A stabilizer of this type is described in Chemical and Metallurgical Engineering, 1934, 41, 589. This emulsifying agent is employed with a small amount of ammonium oleate or soy bean protein. When using this resin, it is desirable to use about 9½ pounds of sodium hydroxide for each 100 pounds of the resin, using considerably higher temperatures, for example about 200° F., when forming the asphalt emulsion.

The concentrated asphalt emulsion is diluted with water in either one of the diluting tanks 18 or 19. The amount of dilution will depend upon the amount of asphalt which is needed in the sheet. In the present instance, the percentage of asphalt in the diluted solution to be used in the impregnating bath will be slightly higher than the percentage of asphalt by weight in the finished sheet. For example, if a finished sheet asphalt content of 8% by weight (based upon the weight of the finished sheet) is desired, the impregnating bath should contain about 10% by weight of asphalt, whereas, if the finished sheet asphalt content is to be as high as 18% by weight, the asphalt impregnating bath should contain about 20% by weight of asphalt.

When forming the diluted emulsion, it is advisable to add a small amount of mold inhibitor, for example sodium pentachlorophenate. A sufficient amount of this material should be dissolved in the diluted mixture to give a 0.4% solution by weight. A small amount of carbon black also may be added, in order to give a sufficiently dark color to the finished material.

After the sheet has passed through the asphalt impregnating bath, it is de-watered to some extent by propelling it through press rolls in a press section 20, and from the press section the sheet which is still wet or damp from the asphalt emulsion bath is immediately conducted

into the second bath 21 which contains the wax emulsion in flame-proofing salt solution. Said wax-salt bath is made in the following manner.

In the dissolving tank 22, there is prepared a solution consisting of 3 parts of ammonium sulfate and 7 parts by weight of water, so that the solution will contain 30% by weight of ammonium sulphate, the active flameproofing substance. It is advisable to inject enough direct steam into the dissolving tank in order to warm up the solution sufficiently to insure complete solution with reasonable rapidity.

The 30% salt solution is then conducted into a mixing tank 23 where it is mixed by vigorous stirring with a wax emulsion containing sufficient wax so that the wax represents about 30% by weight of the amount of active fireproofing salt substance in the solution. Any known appropriate wax emulsion may be used, provided that it is stable in the presence of a strong electrolyte such as the 30% ammonium sulfate solution into which the wax emulsion is incorporated. A wax emulsion with which excellent results have been obtained is one which comprises petroleum wax, a water-soluble gum, and an organic sulfonic acid.

The asphalt-treated, still-damp web, upon passing through the second bath containing the salt and wax impregnant, picks up a substantial amount of said wax-salt impregnant and is then conducted to a large creping dryer 24. The impregnant web is applied to the creping dryer 24 by means of a roll 25 which subjects the web to sufficient pressure to squeeze out excess impregnant.

After the web has passed around the active surface of the creping dryer 24, it is removed by a creping doctor 26, it being understood that at this point the web still contains a very substantial amount of moisture, for example 55% by weight. The creping ratio is not critical. Good results have been obtained with creping ratios of between 1 to 1½ and 1 to 2.0.

The moisture still remaining in the sheet is then removed by drying down to a moisture content representing a normal or stable dry condition for the finished sheet, for example 5% moisture by weight. This drying should be effected without subjecting the sheet to sufficient tension to stretch out the creping, and to this end the web is propelled through a battery of can dryers 27, provided with the usual dryer felt 28. After the creped sheet has been thoroughly dried, it is wound up into a roll 29 by means of any suitable winding arrangement represented as a whole 30.

The composition of the final product, on a bone dry basis and figuring 3,000 sq. ft. of the uncreped material, will be approximately as follows:

|                                 | Per cent |
|---------------------------------|----------|
| Fiber .....                     | 72.2     |
| Asphalt .....                   | 12.0     |
| Flameproofing salts .....       | 12.7     |
| Wax .....                       | 2.4      |
| Sodium pentachlorophenate ..... | .4       |
| Carbon black .....              | .3       |
| Total .....                     | 100      |

It will be understood that the particular ingredients and the percentages of same which are used may be varied in accordance with working conditions, and also in accordance with the purposes for which the sheet is to be used. Ob-

viously, if a high degree of water resistance is desired, it will be advantageous to use a higher percentage of asphalt and of wax, whereas if the sheet must be flame resistant to a high degree, a greater percentage of flameproofing salt will be required.

We claim:

1. The improved process of manufacturing a water and flame resistant paper sheet which comprises the steps of first applying an aqueous emulsion of asphalt to a sheet of paper, then while said sheet is wet with said asphalt emulsion, applying a second emulsion, the continuous phase of which comprises an aqueous solution of a fire inhibiting salt which is a strong electrolyte and the discontinuous phase of which comprises a water resistant wax, and finally drying the sheet.

2. The improved process of manufacturing a water and flame resistant paper sheet which comprises the steps of first applying an aqueous emulsion of asphalt to a sheet of paper in an amount more than sufficient to saturate said sheet, removing excess emulsion from said sheet, then while said sheet is wet with said asphalt emulsion, applying a second emulsion, the continuous phase of which comprises an aqueous solution of a fire inhibiting salt which is a strong electrolyte and the discontinuous phase of which comprises a water resistant wax, and finally drying the sheet.

3. The improved process of manufacturing a water and flame resistant paper sheet which comprises the steps of first applying an aqueous emulsion of asphalt to a sheet of paper in an amount more than enough to saturate said sheet, removing the excess asphalt emulsion from said sheet to reduce the asphalt content to from 4 to 18% by weight based upon the weight of the finished sheet, then while the sheet is wet with said asphalt emulsion applying a second emulsion, the continuous phase of which comprises an aqueous solution of a fire inhibiting salt which is a strong electrolyte and the discontinuous phase of which comprises a water resistant wax, the amount of fire inhibiting salt in said second emulsion being such that said fire inhibiting salt represents from 9 to 16% by weight of the finished sheet and the amount of wax in said second emulsion being such that said wax represents from 1 to 6% by weight of the finished sheet, and then drying the sheet.

4. The improved process of manufacturing a water and flame resistant paper sheet which comprises the steps of first applying an aqueous emulsion of asphalt to a sheet of paper in an amount more than sufficient to saturate said sheet, removing excess emulsion from said sheet, then while said sheet is wet with said asphalt emulsion, applying a second emulsion, the continuous phase of which comprises an aqueous solution of ammonium sulphate and the discontinuous phase of which comprises a water resistant wax, and finally drying the sheet.

5. The improved process of manufacturing a water and flame resistant paper sheet which comprises the steps of first applying an aqueous emulsion of asphalt to a sheet of paper in an amount more than enough to saturate said sheet, removing the excess asphalt emulsion from said sheet to reduce the asphalt content to from 4 to 18% by weight based upon the weight of the finished sheet, then while the sheet is wet with said asphalt emulsion applying a second emulsion, the continuous phase of which comprises an aqueous

solution of ammonium sulphate and the discontinuous phase of which comprises a water resistant wax, the amount of ammonium sulphate in said second emulsion being such that said ammonium sulphate represents from 9 to 16% by weight of the finished sheet and the amount of wax in said second emulsion being such that said wax represents from 1 to 6% by weight of the finished sheet, and then drying the sheet.

EDWARD HUGO VOIGTMAN.  
JOHN CALVIN BLETZINGER.

| Number    | Name         | Date          |
|-----------|--------------|---------------|
| 1,715,080 | Frederickson | May 28, 1929  |
| 2,161,092 | Rowe         | June 6, 1939  |
| 2,314,242 | Porter       | Mar. 16, 1943 |

5

## FOREIGN PATENTS

| Number  | Country       | Date          |
|---------|---------------|---------------|
| 376,407 | Great Britain | July 14, 1932 |
| 519,724 | Great Britain | Apr. 4, 1940  |

10

## REFERENCES CITED

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

15