This invention relates to a composition of matter and to the process of making same and relates especially to a composition adapted for water-proofing various fibrous substances and in particular paper material of various kinds.

This application has derivation in my co-pending applications Serial Numbers 29,258, 101,580, 106,575, 107,461, 286,485 and 394,141 which have matured into Patents Numbers 1,731,194, 1,367,694, 1,739,861, 1,729,582, 1,729,580 and 1,839,088, respectively.

The stock from which the paper product of the present invention is derived may be any suitable wood or rag pulp, fibre and the like, such as sulphite pulp, sulphate pulp, ground wood, rag stock and so forth and suitable mixtures of these. The consistant petroleum hydrocarbons used in augmenting the water resistance of the paper product are preferably of a soft unctuous character such as may be produced, for example, by incorporating paraffin or ceresin wax with various proportions of petroleum oil. In Serial No. 101,580 I have proposed the employment preferentially of a water-white grade of medicinal petroleum oil such, for example, as "Marcol". An oil of this character may be incorporated with a light colored wax to make a consistant mass which when incorporated in paper pulp adds considerably to the waterproofing qualities, tends to improve the texture and also enhances the flexibility so that the paper may be drawn more readily through dyes when a treatment of this kind is required. Various proportions of oil and wax may be used and, as stated in Serial Number 101,580, a proportion of one part of wax to two parts of oil, for example, may be employed. A composition of wax and oil in this proportion yields an unctuous material of ointment-like quality somewhat similar to petroleum. When a wax of a thoroughly amorphous character, such as ceresin, is used the resulting unctuous body has a texture somewhat smoother than when paraffin wax is used.

In the several applications mentioned I have referred to the employment of wax of different kinds and in the present application I may use these same or kindred waxes as desired but preferably employ mineral waxes such as paraffin, ceresin and Montan wax. These solid petroleum hydrocarbons incorporated with a proportion of a petroleum oil somewhat greater than the amount of wax yield as indicated unctuous bodies of varying degrees of hardness or softness. This invention, therefore, comprehends petroleum wax softened with petroleum oil to such a degree as will form substantially an unctuous mass.

In the manufacture of paper of various grades, but particularly those light in color, I prefer to employ refined waxes and oils free from any high degree of coloring matter which if present would tend to discolor the paper and deprecate its market value. However, I do not limit myself to the use of medicinal grades of petroleum oil such as Nujoil or Marcol but may employ various other liquid petroleum hydrocarbons such as those of a lubricating oil type, spindle oil, and the like. In many cases paper substantially free from odor is required and the use of oils of low grade possessing considerable odor is undesirable. For papers which are required substantially free from odor I therefore employ a deodorized petroleum oil.

In Serial 101,580 I have set forth the utility of hydrocellulose in paper pulp employed with wax or wax and oil waterproofing material and in the present invention I may likewise employ hydrocellulose to any desired degree.

The consistant petroleum hydrocarbon mixture preferably is introduced into the paper pulp as a dispersion or emulsion. Such dispersions may be prepared in various ways as, for example, by dissolving one or two ounces of ordinary soap in a gallon of water and mixing this with the unctuous hydrocarbon mixture, the latter preferably being heated slightly above its melting point. Equal proportions by volume of the soap solution and the unctuous material in admixture are passed through a colloid mill or other suitable dispersing or emulsifying device to yield a dispersion which may be diluted with water as required for addition to the paper pulp.

The dispersion may be added to the pulp in the beater engine at any stage of the operation of heating, but preferably is introduced when the beating has been substantially completed. Or the dispersion may be introduced into the Jordans or at the screens. Hence at some stage prior to the formation of the paper pulp into a sheet the dispersion is added in an amount sufficient to have present in the dried pulp stock a quantity of the unctuous waterproofing agent, say from two to five per cent on the dry weight of the paper. This range, however, does not place any limitation upon the amount of unctuous waterproofing agent incorporated, as certain conditions or requirements may demand the employment of a greater or lesser amount of the waterproofing agent.

In some cases the dispersion of the unctuous
waterproofing agent, before incorporating with the pulp at any suitable stage, may be treated with alum, calcium chloride, hydrochloric or sulfuric acid, or any other agent reactive with sodium silicate, to alter the hydrogen ion value of the dispersion in order to make it conform in any suitable way with the pH value of the pulp. In other cases the dispersion may contain sodium silicate and a precipitant such as alum may be added to the dispersion prior to incorporation with the pulp in order to precipitate the ionic hydrocarbon particles. Again, the dispersion may be added to the beater or elsewhere without such preliminary neutralization, precipitation or similar treatment and the setting of the ionic particles brought about in the presence of the pulp by the addition of alum or other precipitant.

In producing paper in this manner the employment of resin size and the like is not precluded, although not ordinarily recommended from the standpoint of increased water resistance as the ionic dispersed ionic particles throughout the paper structure may be expected to produce in the paper an adequate degree of waterproofing or resistance to water penetration without the presence of the usual paper sizing and at a cost ordinarily lower than can be secured by the use of resin size.

The paper pulp having been treated in this manner is run onto the usual paper-making machine to produce paper, board and similar products. It may be hot calendered if desired to further impregnate and disseminate the ionic mass throughout the paper tissues. Heavier paper or board may be built up in layers, in which case it will be found feasible to apply the ionic waterproofing dispersion to one or more layers only, if desired, in order to reduce the cost of the ionic material present with consequent saving in cost. Water then may penetrate through those layers which are not so treated but will not pass readily through the layer or layers treated with the ionic waterproofing dispersion.

In Serial Number 101,580, I have referred to the employment with various waxes, such as paraffin, creosin, Montan, carnauba, Japan, beeswax, and the like, alone or admixed with resin, various oils and so forth, of additions of starches.

I may employ with the present wax-containing compositions, particularly those of an unctuous character, various proportions of starches, such as wheat starch, corn starch, cassava starch, and the like. The starch is preferably dissolved in water and the mixture of the starch solution and the waterproofing agent, preferably hot, is then emulsified as, for example, by forming a dispersion with the aid of a colloid mill. A very high degree of dispersion may be obtained in this manner.

The sizing compositions prepared in accordance with the present invention may also be employed with sizing compositions that contain oxidized hydrocarbons and particularly oxidized waxes. As examples of oxidized hydrocarbons and waxes that may be utilized, there may be mentioned paraffin wax, and other waxes such as carnauba, candleilla, Montan, ceresin, and the like. Blown hydrocarbons, such as blown petroleum oils, may also be utilized, and mixtures of the blown waxes with oils, or of the blown waxes with blown oils, or of waxes with blown oils, or of any combination of these ingredients may be employed in connection with the present invention. The waxes may be oxidized and then incorporated with oils to soften the waxes, or the waxes and oils may be simultaneously submitted to an oxidation to produce the desired products. In the preparation of paraffin wax, whatever oxidized hydrocarbons are employed should be of substantially non-pigmenting power, so that the paper will not be substantially discolored. In such instances, therefore, substances such as blown tars, blown asphalts, and the like, which would be of a contaminating character and which would be dark in color and would accordingly discolor the paper, are avoided. However, in those cases where discoloration or dark coloration is of relatively minor importance, such darkened oxidized materials may be utilized. As stated, however, the preferred instances involve the use of oxidized hydrocarbons which are substantially light in color, and free or substantially free from undesirable odor, and which do not impart any objectionable taste to any food material when the paper is used in contact therewith. For example, where the oxidation of paraffin wax is carried to a stage where dark colored resinous substances or strongly odoriferous aldehydes and the like result, these when present in paper used in packing foodstuffs may exert a contaminating influence. For such purposes, therefore, it is preferred to keep the oxidation to a stage where resinous substances substantially are not formed, and the physical appearance of the wax which has been subjected to incipient oxidation is only very slightly altered.

As an example of an oxidized wax that may be employed, oxidized paraffin may be prepared by blowing a current of air or oxygen, or other oxygen-containing gases, through the molten material for a period of several hours, the temperature usually ranging from 160°-200° C. Oxygen goes into combination with the fatty acids to form a product which has been thus subjected to incipient oxidation results which is desirably employed in carrying out the purposes of the present invention.

The oxidized wax in a stage of incipient oxidation is mixed with pulp, preferably in the beater engine, or any other suitable stage in advance of actual formation into a sheet. Two or three per cent by weight of the blown wax, based on the paper material, may be introduced advantageously in this manner. Wax in this proportion, or even lesser relative amount creates a desirable waterproofing effect. The paper stock may be any ordinary paper stock, such as is illustrated above.

Difficulty has arisen in the past in the endeavor to use paraffin wax in paper pulp due to clogging of the felts and screens with wax. In the present invention, it is proposed to oxidize the wax to a stage sufficient to render its dispersion in water very thorough and permit of more effective utilization of these ingredients. The oxidized wax may be employed with the dispersed blown wax by the wet paper pulp. The exact degree of waterproofing or water resistance created depends
however on the requirements of service conditions, and in some cases a waterproofing effect of comparatively light degree may be all that is required, while in other cases, a much more substantial degree of wax resistance is needed. The blown wax, therefore, should be used in such proportions as meets the specific requirements in hand.

The blown wax may be used in conjunction with rosin size or other paper sizing agent. Aluminum, aluminum hydrate, and various other coagulating agents for size may be used, as required. If the coagulating agents are used together with the sizing material prior to the incorporation of the sizing composition into the pulp in the beater, a preset sizing agent will result. Such preset compositions offer advantages, but on the other hand, the sizing compositions may be employed in the usual manner with the coagulating agents added after the sizing composition has been incorporated into the pulp.

Instead of using a harder and more expensive grades of paraffin wax, it is possible to use various cheaper grades of wax including scale wax, or wax which has been softened with various oils. Thus in some instances it is preferred to employ the emulsion or dispersion of a mixture of wax in a good grade of petroleum oil, such mixture being air-blown to at least a state of incipient oxidation. For a very high grade of wax paper there may be employed a blown mixture of wax and one of the so-called medicinal petroleum oils, in which produces oil such as "Nujol" or "Marcol" are typical. For lower grades of paper, especially when color is not important, various petroleum oils admixed with wax may be blown to yield an oxidized product which when dispersed in an aqueous medium may be readily incorporated in the wet paper pulp.

The waxes themselves may be blown or mixtures of the waxes, or mixtures of waxes with oils, may be oxidized simultaneously. For example, a mixture of waxes may be simultaneously oxidized and a disperser prepared from such composite oxidized waxy material. Thus paraffin wax with 5 to 10 per cent of Montan wax may be blown with air at a temperature of say, 170°C for five hours. In the manner, blown mixtures of paraffin wax, petroleum oil and Montan wax or other wax of a character different from paraffin wax may be blown and thus oxidized. Thus blown ceresin or unctuous mixtures of a petroleum wax such as ceresin with a petroleum oil may be utilized.

The dispersion of the oxidized material may be made in various ways, preferably with the aid of one or more emulsifying agents such as soap, stear, benzine, silicate of soda, and the like. Thus a few per cent of stearic or oleic acid may be melted with the oxidized paraffin and this composition emulsified with a hot, dilute, aqueous solution of caustic soda or ammonia. The ammonia composition is preferable in some cases because ammonia may be removed very readily. Or, silicate of soda may be incorporated with the oxidized material and sufficient water to produce a creamy dispersion, and the mixture passed through an emulsifying apparatus such as a colloid mill with the result a colloid may be produced.

The amount of dispersing agent may be quite small. This is advantageous when ordinary soaps are employed because these tend to produce foaming in the beater and therefore the proportion of these should be kept at a minimum. Less than 1 per cent of potassium or sodium oleate may be employed to make a satisfactory dispersion of oxidized paraffin wax in water. The dispersion may contain about 80 per cent of wax and yet be readily handled.

As indicated above, the oxidized paraffin emulsion may be added to the beater engine which advantageously may be done at the time the paper stock is charged thereto. After thorough mixing in the usual manner in the beater a quantity of resin size or any other desired sizing agent may be added and such size set in the usual manner with alum or with any other setting agent. The addition of resin size or similar sizing agents of paper, it being proposed to produce paper with a sizing agent of a resinous character, if so desired, employing solely the oxidized material aforesaid to create adequate water resistance for the purpose in hand.

A paper pulp which contains a substantial proportion of hydrocellulose is advantageous in assisting in the fixation of the oxidized wax. The hydrocellulose may be added to the pulp or formed in it in any suitable manner.

The invention may be illustrated by the following:

A mixture of equal parts by weight of sulphite pulp and ground wood is agitated in water in the beater with a dispersion of oxidized paraffin wax sufficient to introduce about 4 per cent of wax into the finished paper. The dispersion of the blown wax is made by violent agitation of equal volumes of the wax and a 1 per cent solution of sodium or potassium oleate. Agitation in the beater is continued until hydrocellulose is formed to a considerable extent. After thorough mixing in this manner, rosin size is added sufficient to introduce 1 or 2 per cent of resin or rosinate and this rosin size is set by alum, either already present in the beater, or added after the rosin size has been incorporated. The proportion of alum introduced is sufficient to react both with the alkali of the rosin size and with that of the sodium or potassium oleate employed in dispersing the blown wax.

The pulp so treated is formed into a sheet of paper which may be of single layer construction or may be built up in the paper machine in several layers to form a board. Whether in a single sheet or single layer form or built up in a plurality of layers, I include under the designation sheet paper these and other varied forms of sheeted paper pulp.

The sheet is then calendered, preferably hot, and the particles of oxidized wax, oxidized oil, and so forth, are thus further disseminated through the fibrous mass (and into the fibres thereof) composing the sheet. In this way an enhanced degree of water resistance is obtained.

The procedure of the foregoing illustration may be varied in different ways, as for example, a cheaper paper stock may be made by utilizing 3 parts by weight of ground wood to 1 part of sulphite or sulphate pulp. The oxidized waterproofing material may be a blown mixture of paraffin containing 10 to 20 per cent of hydrocarbon oil. The employment of the blown hydrocarbon oil may be desirable in operations where the paper is to be printed. In other words, the illustration set forth depicts merely one procedure and since numerous variations are possible, it is to be understood that the invention is not restricted in any manner by the specific character of the illustration.

In the illustration set forth above 4 per cent of 75
the oxidized waxy material is recommended. This is a high proportion for many purposes and 1 or 2 per cent of the blown material may be used advantageously in such cases. On the other hand, for making waxed paper and using blown wax, I may increase the proportion to produce the desired waxed effect.

It should be understood that I am not precluded from adding unoxidized oils and waxes to the blown wax or blown mixtures of hydrocarbons, when for any reason such admixture is desired, as for example, to cheapen the product.

Reference has been made above to the desirability of adjusting the hydrogen ion value of the dispersion in order to make it conform in any suitable way with the pH value of the pulp. It is preferred to employ a pulp which has been brought substantially on the acid side, that is one having a pH value of less than 7 but not substantially less than 1.5, since too great an acidity is harmful since it is apt to break down the emulsion and cause coagulation of the colloidal dispersed wax particles, whereby proper absorption does not occur. The particular hydrogen ion concentration of the pulp varies for different conditions and stocks being treated. A preferred range of hydrogen ion concentration of the stocks when wax sizing compositions are employed may be stated to lie between 7.2 to 5.5. With ordinary rosin sizes, the pH of the stock is preferably maintained within the limit of 4.5 and 5.0. The utilization of wax dispersions, therefore, enables a stock to be employed in which the hydrogen ion value is not as critical as when the ordinary rosin sizes are employed. Accordingly, depending on the particular hydrogen ion concentration of the stock employed, the dispersion or emulsion may have its pH value altered to conform in any suitable way with the pH value of the pulp.

Having thus set forth my invention, I claim:

1. A paper sizing composition comprising a blown mixture of wax and petroleum oil.
3. A paper sizing composition comprising an aqueous emulsion of an oxidized petroleum wax and a hydrocarbon oil.

CARLETON ELLIS.