This invention relates to paper products and to the process of making same and relates especially to paper material of increased water resistance due to the presence of petroleum hydrocarbons of a consistent character disseminated through its structure.

This application has derivation in my co-pending applications Serial Numbers 29,268 filed May 20, 1925, 101,580 filed April 12, 1926, 106,575 filed May 3, 1926, 107,451 filed May 7, 1926 and 286,488 filed June 18, 1928.

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 consistent petroleum hydrocarbons used in augmenting the water resistance of the paper product is 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 consistent 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 petroleumum. 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 depreciate its market value. However, I do not limit myself to the use of medicinal grades of petroleum oil such as Nujol 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 Number 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 consistent petroleum hydrocarbon mixture preferable 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 beating, but preferably is introduced when the beating has been substantially completed. Or the dispersion may be introduced into the Jordon 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 percent 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 sulphuric acid, or any other agent reactive with soap 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 pre-set the unctuous 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 unctuous 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 rosin size and the like is not precluded, although not ordinarily recommended from the standpoint of increased water resistance as the disseminated unctuous 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 rosin 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 disperse the unctuous mass through the paper tissues. Heavier paper or board may be built up in layers in which case it will be found feasible to apply the unctuous waterproofing dispersion to one or more layers only; if desired, in order to reduce the amount of the unctuous 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 of layers treated with the unctuous waterproofing dispersion.

In Serial Number 101,580, I have referred to the employment with various waxes, such as paraffin, ceresin, 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, cornstarch, 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.

What I claim is:

1. A paper product containing a disseminated unctuous petroleum hydrocarbon mixture serving as a water resisting agent.
2. A paper product containing a consistent hydrocarbon waterproofing agent comprising an amorphous wax and a petroleum oil.
3. A paper product containing a consistent hydrocarbon waterproofing agent comprising ceresin and a petroleum oil.
4. A paper product containing a consistent hydrocarbon waterproofing agent comprising ceresin wax and a white medicinal petroleum oil.
5. In the process of making paper, the step which comprises incorporating with the paper pulp a dispersion of an unctuous petroleum hydrocarbon mixture and forming the pulp into sheet material.
6. In the process of making paper, the step which comprises incorporating with paper pulp a dispersion comprising an unctuous mixture of a petroleum wax and a petroleum oil.
7. In the process of making paper, the step which comprises incorporating with paper pulp a dispersion comprising consistent petroleum hydrocarbons of a substantially unctuous character.
8. A paper product containing a water-resisting agent comprising a disseminated unctuous hydrocarbon mixture obtained from a dispersion containing the same in an amount of approximately 2-5% on the dry weight of the paper stock.
9. A paper product containing a water-resisting agent comprising an amorphous wax and a petroleum oil the amount of the oil ex-
ceeding that of the wax in the composition.

10. In the process of making paper, the step which comprises incorporating with paper pulp an unctuous hydrocarbon mixture in an amount of approximately 2-5% on the dry weight of the paper stock.

11. In the process of making paper, the step which comprises incorporating with paper pulp an unctuous hydrocarbon mixture containing an amorphous wax and a petroleum oil, the amount of the oil exceeding that of the wax in the composition.

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