The present invention relates to sheeted, fibrous materials embodying multi-axial fiber assemblies of amorphous plastic foamed resins, and processes for the manufacture thereof. The invention particularly includes paper, paperboard and pulp stocks composed of disintegrated urea-formaldehyde foamed resin in admixture with fibrous materials of the kind normally employed in the manufacture of paper products.

Paper, as it is generally known today, is composed of matted or felted cellulosic fibers, such as those obtained from wood, cotton, bagasse and similar vegetable sources. For certain special applications, a portion of the paper-making cellulosic fibers may be replaced by mineral fibers, for example, vitreous fibers, or filaments of synthetic resins generated by a wet-spinning process, including regenerated cellulose, cellulose acetate, polyesteramides, polyvinyls, acrylonitriles, polyvinyl acetate-chloride copolymers. These heterogeneous stocks are, however, limited in their compositions by the ability of the substituted ingredients to fibrillate under the mechanical action of beating in order to accentuate the bonding forces between fibers, although in some cases bonding agents may be included in the stock or with some synthetic resin filaments, a heat treatment after web-formation can result in a physical union of the fibers.

The usual fiber found in a paper stock, whether mineral, vegetable or synthetic resin is uniaxial or uni-dimensional in character, wherein the ratio of length to diameter or width has an order of magnitude of from 10 to 1 to 100 to 1. The geometry of these fibers and the mechanics by which they are formed into paper, naturally tends to make the predominance of the fiber axes assume such positions that they lie in the plane of the resultant sheet, with, of course, some overlapping and/or interlacing. Where it has been desired to modify the physical aspects of the paper, slurries of greater density may be utilized to form a thicker sheet and with less compression during drying a bulkier product is enabled. Creeping of the sheet as it is removed from the machine or an embossing, scoring or perforating step during finishing operations will also serve to disrupt the normal uniplanar sheet formation.

It is an object of our invention to provide a sheeted, paper-like material from a heterogeneous mixture of uniaxial and multi-axial fibers which enables generation of a “flocked” product possessing surface characteristics resembling those of plied fabrics.

Another object of the present invention is the provision of a sheeted, paper-like material from a mixture of cellulosic fibers and multi-axial fiber assemblies of a foamed synthetic resin possessing inherent physical bonding forces.

A further object of the present invention is to provide means whereby easily fibrillated wood fibers may be combined with multi-axial assemblies of fibers of a non-fibrillating type of synthetic resin and united in a strong, felted sheet possessing a high bulk and opacity.

Still another object of our invention is to provide a sheeted, light weight paper product containing a disintegrated urea-formaldehyde foamed resin.

Other objects and advantages of the present invention will be readily apparent from the following description of certain preferred embodiments thereof, when taken in conjunction with the accompanying drawing, wherein the single figure is a diagrammatical representation of a photomicrograph, at 400 diameters, illustrative of the comparative geometric configurations of the resin fragments and the cellulosic fibers combined in the products of the invention.

Briefly stated, the present invention contemplates the inclusion in conventional paper stocks of multi-axial fiber assemblies of a disintegrated urea-formaldehyde resin foam whereby to alter to a substantial degree the physical characteristics of the ultimate paper products.

It has been discovered that certain synthetic resins can be converted into semi-rigid foams, with structures of definite geometry. A urea-formaldehyde prepolymer, for example, formed by condensing urea and formaldehyde in an approximate 1 to 2 molar ratio, can be foamed by addition to a cellulated mass of a surface active agent, water and an acid catalyst such as sulfuric acid. Regulation of the density of the cellulated matrix by aeration thereof enables control of the density of the resin foam within limits of from 0.2 to 0.8 pound per cubic foot. Additionally, it has been noted that the degree of sintering and matrix agitation affects the fineness of the ultimate foam which can have as many as $10^6$ cells per cubic centimeter. Upon curing and drying, there will be observed some possible collapse or retraction of the cell structure having a skeletal configuration composed of red-like strands and assemblies, which under agitation may be disintegrated into segments and cell residues of various degrees of complexity and finally into branched or multi-axial fiber nodes comprising broken residual junctions of the original foam structure. Melamine-formaldehyde, urea-formaldehydes, melamine-urea-formaldehyde resin foams and products with formaldehyde may be similarly processed to produce light weight foams.

Disintegration of the resin foam may be effected in conventional hydrocyclones, beaters, jordans, fiberizing disc mills and the like, equipment usually employed in the preparation of wood fiber pulps. The degree of disintegration, deagglomeration or foam fracture will depend upon the nature of the apparatus utilized and the time of exposure. Manifestly, vigorous agitation under increasing increments of pressure will result in more disintegration than would be possible when operating at low pressures for short periods of time. It is, of course, conceivable that the resin foam particles with the beating of the wood pulp and the blending of the cellulosic and resin fibers preliminary to the sheet formation. The type as well as the amount of uniaxial fibers with which the disintegrated resin foam is combined may be varied within wide limits as desired and will, of course, determine the nature of the ultimate paper which is formed. Cellulosic fibers from soft and hard woods, bagasse, bamboo, cotton are suitable source materials and the treatment thereof may include sulfite, sulfate, semi-chemical as well as chemi-mechanical pulping. Where a wood base is employed, groundwood pulps are quite appropriate. Although mineral fibers can replace a portion of the cellulosic fibers in the base pulp, it is preferred that these be in the minority in order to obviate the need of special bonding additives in the ultimate sheet formation. Similarly, the presence of a small percentage of uniaxial filaments of a spun synthetic resin is also contemplated. It is preferred that the uniaxial cellulosic fibers constitute the major portion of the paper stock, although as much as 50% by weight of such stock may be composed of the disintegrated resin foam.

The invention will be more particularly described with reference to the following examples which are intended for purposes of illustration only.
Example I

A weight of 324 grams of commercial formalin solution (37% formaldehyde) was treated with 20 grams of pyridine in a 1-liter, 3-necked flask equipped with mechanical stirrer and condenser turned down for distillation. One hundred fourteen grams of urea and 7.6 grams of thiourea were added. The solution was heated to boiling and distilled at atmospheric pressure. A volume of 165 ml of distillate was obtained over a period of about two hours. The residual solution was cooled to room temperature. It was of medium viscosity and had a cloudy appearance.

This resin solution was foamed as follows:

Three ml of Nornemipin-N (an alkylated naphthalene sulfonic acid surface active agent) were dissolved in 50 ml of water. A volume of 1.5 ml of 85% phosphoric acid was added and the solution whipped into a foam at room temperature using a Sunbeam Mixmaster. Air was bubbled into the foam in the beginning to facilitate the foaming. After a large volume of uniform foam was obtained, 50 grams of the above aqueous resin solution were added slowly with simultaneous whipping. The pH of the foamed mixture measured about 2. Whipping was continued until the foam set which required about ten minutes of whipping after all of the resin solution had been added.

The foam was transferred to an aluminum foil-lined pan and permitted to stand at room temperature for about two hours. It was then dried in a forced-draft oven at 60°C for five hours. The dried foam was white and had a soft and resilient texture. The density of the foam was 0.8 pound per cubic foot.

Example II

A foamed resin was produced in accordance with the disclosure of British Patents 768,562 and 773,809. The density of the resultant foam was 0.3 pound per cubic foot, although its texture and physical appearance were in other respects substantially identical to that of the foam of Example I.

Example III

The foam of Example I was disintegrated and/or deagglomerated by agitation in a British Standard Disintegrator in water suspension at 75°C and at 1% consistency for various periods of time from 30 seconds to 60 minutes. At the end of 30 seconds the foam comprises essentially fractured three-dimensional networks with only traces of branched three-dimensional rods. This degree of deagglomeration is satisfactory for the production of paper possessing exceptionally high bulk. Disintegration for five minutes produces a slurry composed of a mixture of branched three-dimensional rod-like structures and linear assemblies containing but a small quantity of the three-dimensional networks of the original reticulated foam. Further disintegration increases the amounts of three-dimensional rod-like structures and enables the production of paper possessing satisfactory physical properties such as opacity, texture, softness and appearance.

Example IV

A weight of 1.5 grams of urea-formaldehyde resin foam of Example II was comminuted by hand and added to 742 ml of a sulfitc wood pulp suspension of mixed western hemlock and white fir having a consistency of 1.4% and a freeness of 365. The admixture was diluted with water to 2000 ml and then blended under vigorous agitation for five minutes. In another preparation 4.5 grams of resin foam were combined with 577 ml of wood pulp suspension and similarly processed. British hand sheets were prepared using 400 ml of suspension for each sheet. The sheets, as shown in the drawing contained fractured or branched three-dimensional rod-like fragments of disintegrated resin foam together with some few particles of resin foam and cellulosic fibers, were per-

mittied to dry over night at 75°F and 55% relative humidity and were then tested. Results are as follows:

<table>
<thead>
<tr>
<th>Dry Basis Weight</th>
<th>Sy. Vol.</th>
<th>Brightness</th>
<th>Breaking Length</th>
<th>Tear Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Pulp</td>
<td>162</td>
<td>75.9</td>
<td>6.194</td>
<td>142</td>
</tr>
<tr>
<td>90% Pulp-10% Resin</td>
<td>145</td>
<td>82.5</td>
<td>2.484</td>
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The foregoing results indicate the resin inclusions improve the bulk of the sheeted paper together with an increase in the brightness thereof, properties which are of particular value to such products. Unmeasurable physical properties ascertainable only upon inspection present in papers modified by the resin inclusions are increased softness, enhanced surface attractiveness and feel. Similarly, resin inclusions increase sheet opacity in direct proportion to the resin content thereof.

It has also been ascertained that the inclusion of assemblages derived from disintegration of foamed aminoplast resins in paper stocks will improve the absorbencies of ultimate paper products and, moreover, the rate at which these absorbencies decrease with age is greatly reduced. These resin inclusions also result in increased air entrapment within the sheeted paper, thus leading to products containing excellent thermal barriers. The insulating quality of the composite sheeting will be dependent to a large extent upon the degree of disintegration of the foamed resin employed therein. Where necessary, or desirable, the high bulk, insulating and/or absorbptive paper of our invention may be laminated to thermoplastic film material in order that there will be estimated an impervious skin or layer upon the composite sheeting and its utility as an insulating medium will be increased.

The high bulk papers of our invention are acceptable substitutes for the conventional papers of modern commerce and the development of a novel source of papermaking fibers, that is, disintegrated foams and more especially disintegrated aminoplast resin foams enables the generation within the ultimate paper products of properties which impart to such products considerable commercial potential.

It will be understood that the paper products of the present invention may be modified by the inclusion therein of other per-forming fibrous materials, sizes, impregnating agents, coating materials, fillers, wet strength resins commonly encountered in paper manufacture. Additionally manifold variations in compositions and procedural details of their formation are possible without departing from the spirit of the invention or the scope of the appended claims.

What we claim is:

1. A paper characterized by high bulk comprising a basis of uni-axial fibrous material having uniformly admixed therewith three-dimensional, multi-axial assemblies containing the cell wall structure of partially disintegrated, cured aminoplast resin foam having a density below 0.8 pound per cubic foot.

2. A paper characterized by high bulk comprising a basis of uni-axial fibrillated fibrous material having uniformly admixed therewith three-dimensional, multi-axial assemblies containing the cell wall structure of partially disintegrated, cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot.

3. A paper characterized by high bulk comprising a basis of uni-axial fibrillated cellulosic material having uniformly admixed therewith three-dimensional, multi-axial assemblies containing the cell wall structure of partially disintegrated, cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot.

4. A paper characterized by high bulk and opacity comprising a basis of uni-axial fibrillated wood pulp having uniformly admixed therewith multi-axial fiber as-
ssemblies containing the cell wall structure of a partially disintegrated cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot.

5. A paper characterized by high bulk and opacity comprising a basis of uni-axial fibrillated bleached sulfite pulp prepared from western hemlock and white fir having uniformly admixed therewith multi-axial fiber assemblies containing the cell wall structure of a partially disintegrated cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot in an amount of from 1 up to about 30% by weight of the total mixture.

6. A process of making a paper of high bulk which comprises combining a uni-axial fibrous material with three-dimensional, multi-axial assemblies containing the cell wall structure of a partially disintegrated, cured aminoplast resin foam having a density below 0.8 pound per cubic foot and converting said admixture into sheetlike form.

7. A process of making a paper of high bulk and opacity which comprises combining a uni-axial cellulosic material and a partially disintegrated cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot, in an aqueous suspension, beating said combination to fibrillate the cellulosic material and to convert the partially disintegrated foam into the form of multi-axial fiber assemblies containing the cell wall structure of the foam which assemblies are capable of a physical bonding with said cellulosic material, and sheeting said combination.

8. A process as defined in claim 7 in which the foam assemblies constitute from about 1 to about 30% of the weight of the sheeted paper.

9. A process of making a paper of high bulk and opacity which comprises partially disintegrating a cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot in aqueous suspension into a plurality of multi-axial fiber assemblies containing the cell wall structure of the foam, combining said suspension of foam fiber assemblies with a slurry of uni-axial fibrillated wood pulp, blending said combination to substantial homogeneity and thereafter sheeting said combination.

10. A paper stock comprising a basis of uni-axial fibrillated fibrous material having uniformly admixed therewith three-dimensional, multi-axial assemblies containing the cell wall structure of a partially disintegrated, cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot.

11. A process of making a paper stock which comprises combining a uni-axial cellulosic material and a partially disintegrated, cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot in an aqueous suspension and beating said combination to fibrillate the cellulosic material and to convert the foam into multi-axial fiber assemblies containing the cell wall structure of the foam, which assemblies are capable of a physical bonding with said cellulosic material.

12. A paperboard comprising a basis of uni-axial fibrillated fibrous material having uniformly admixed therewith three-dimensional, multi-axial assemblies containing the cell wall structure of a partially disintegrated, cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot.

13. As a component of fibrous stock adapted to the production of sheet material, three-dimensional multi-axial assemblies containing the cell wall structure of a partially disintegrated, cured urea-formaldehyde resin foam having a density below 0.8 pound per cubic foot.

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