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OIL ABSORBENT, OIL RESISTANT IMPREGNATED PAPER

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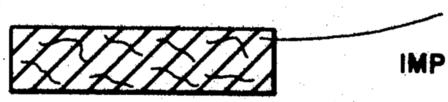

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OIL ABSORBENT, OIL RESISTANT IMPREGNATED PAPER

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ABSTRACT OF THE DISCLOSURE

An oil resistant, flexible absorbent paper product which is capable of absorbing two to three times its own weight without disintegration. The paper has a strengthening impregnant of a styrene-butadiene polymer including a minor proportion by weight of an epoxy resin sufficient to cross-link the styrene-butadiene. The process of impregnating the absorbent cellulosic web includes impregnation by the styrene-butadiene and the epoxy in emulsion systems.

This invention relates to elastomer saturated paper and particularly to methods of producing such papers having good flexibility and stretch properties as well as resistance to deterioration by organic solvents including attack by hydrocarbons.

Paper is commonly impregnated with elastomeric materials for a variety of purposes. One such representative purpose is as a base sheet in a pressure sensitive tape. In such tapes the impregnated sheet serves the purpose of providing strength to the tape composite. The elastomeric impregnated material is commonly cured. Known impregnants for such base sheets which are subject to curing include terpolymer materials such as styrene-butadiene compositions having functional groups which include active hydrogen or the like. A common deficiency of such elastomer saturated papers is that the necessary curing action not only improves the strength but it decreases the flexibility and stretch properties of the material. Furthermore, such materials as the terpolymer compositions noted are not normally resistant to attack by organic solvents.

It is a purpose of this invention to provide an impregnated paper web in which the strengthening impregnant of the web is a terpolymer and which impregnated web demonstrates a material resistance to attack by hydrocarbons including oils and solvents such as xylene, toluene and the like. It is another object of this invention to provide a novel method of impregnating a cellulosic web to attain desirable physical characteristics in the product by the inclusion in the impregnant of only a very minor quantity of an epoxy type resin serving basically as a curing agent.

I have found that, if a small percentage of an epoxy resin is included in the elastomeric formulation for the impregnation of a cellulosic web, the above noted objects of this invention may be achieved. Specifically, the product is oil resistant and through, in fact, it may absorb some significant quantity of oil and undergo some slight swelling, it will not disintegrate mechanically. Additionally and quite surprisingly, despite the fact that the epoxy apparently serves as a cross-linking agent for the styrene-butadiene terpolymer and would be expected to render the product relatively rigid, the stretch characteristics and flexibility of the cured impregnated material are, in fact, similar to those of the uncured sheet.

The styrene-butadiene employed in the practice of the invention is a common type but characterized by the presence of functional hydrogen. Carboxylic styrene-

butadiene is one terpolymer which serves the purpose and may be formulated with styrene, butadiene and acrylic acid. While it is convenient to employ the carboxylic styrene-butadiene since they are readily commercially available polymers of styrene-butadiene having active hydrogens, other systems with active hydrogen may be employed. Such include as functional groups the amines and amides. Commonly, I prefer to employ terpolymers of carboxylic styrene-butadiene in which the styrene is present (dry basis by weight) between about 20 to 40%, the acid 1 to 3%, and butadiene is the remainder.

The epoxy resins which I prefer to employ are those which are of a relatively low molecular weight and dispersible in water or readily emulsifiable. Epoxy resins which serve the purpose well include the di-epoxides, for example, which are commercially available colorless to pale liquids having a viscosity of about 90 to 150 centipoises at 25° C., a neutral pH and a gallon weight of about 10.2 pounds. Higher molecular weight resins may be conveniently dispersed in solvents prior to their emulsification and, accordingly, both liquid and solid type materials are useful. One commercially available resin having an epoxide equivalent at about 185–192 and an average molecular weight of about 380 and which is readily dispersible in hydrocarbon solvents such as toluene and xylene is also useful for the purpose.

The invention will be more fully understood by reference to the following example and accompanying drawing wherein the single figure is a sectional view illustrating a base sheet impregnated in accordance with the invention.

The following example provides comparative data on materials produced with from zero to 5% epoxy (dry weight percent based on rubber dry weight).

The cellulose web for the comparative purpose comprised a saturating base sheet of essentially 100% kraft pulp. This base sheet was impregnated with the combined emulsion system formed as described below. After impregnation, as by dipping in the emulsion, the web was then squeezed to a pickup on a dry basis of 45 parts of the impregnant per 100 parts by weight of base sheet.

A first emulsion was made up in conventional fashion and is here conveniently termed "Emulsion A." This emulsion was a commercial material and as purchased contained on a solids basis:

	Percent
Butadiene	72
Styrene	25
Acrylic acid	3

A second aqueous emulsion was prepared from a bifunctional epoxy resin and a non-ionic emulsifier, in this case polyoxyethylene sorbitan trioleate. The epoxy resin is the dispersed phase. The aqueous or continuous phase may include only water but, if desired, other components such as antioxidants, emulsion stabilizers and viscosity control agents may be included, for saturant stability. In the present instance the emulsion contain an epoxy resin with an epoxide equivalent of about 150 and a density of 1.2 gm./cm.^{3}.

This second emulsion, conveniently termed "Emulsion B," was prepared as follows:

	Parts
Epoxy resin	20
Polyoxyethylene sorbitan trioleate	1
Water	100

Such components are emulsified with an Eppon bach mixer. When emulsification had been completed, the epoxy emulsion—"Emulsion B"—was added to styrene-butadiene emulsion—"Emulsion A"—in three different proportions having a dry weight ratio of rubber to resin of 100:0.5;

100:1; and 100:5 respectively. After dipping and squeezing, as already noted, cure of these low density impregnated cellulose webs was effected in an oven at about 115° C. (239° F.) for three hours. In all cases the rubber to cellulose ratio was 45:100.

Curing time is inversely related to temperature, and the system has been cured at temperatures of between about 70° F. and 300° F.

The cured impregnated base sheets were tested and compared with a similar base sheet lacking the epoxy resin by subjecting the sheets to a liquid hydrocarbon as follows: strips were saturated with motor oil (20 A.S.E.) and tested on an Instron tester, the rate of elongation being 4%/min.

Amt. of epoxy resin/100 parts rubber	Tensile (lbs./15 mm.)	Stretch, percent	Tensile-energy-absorption (inch-pounds)
0	3.8	5.6	0.786
0.5	4.7	5.8	0.964
1.0	4.7	5.6	0.918
5.0	5.0	4.9	0.856

As will be noted from the foregoing exemplary data, the epoxy inclusion appears particularly effective in the low ranges. Frequently 0.5 to 1% dry weight based on the rubber is sufficient for the purpose. I have found that between about ½ part to 5 parts by weight per 100 parts of dry rubber is generally useful and more than 5 parts is not commonly necessary or economical. Additionally, I have found that the physical characteristics of sheets varying in epoxy content but not subjected to oil vary but little in tensile, stretch and the like. It is when subjected to the oil that the effects of the epoxy inclusion are noted. The physical properties of the product will vary somewhat, of course, with the degree of impregnation—most suitably, the impregnant by weight is present to the extent of about 30 to 120 parts per 100 parts of fiber. But varying the impregnation does not contribute to the product in the same manner as the epoxy. In brief, the sheets, whether or not they contain the epoxy, will tend, because of their structure and porosity, to absorb oil. This is occasioned by the very low density and the exposed rubber covered, substantially individual fibers. The presence of the epoxy, however, precludes the disintegration of the impregnated sheet with oil absorption because the rubber is much less swollen by a given amount of oil absorbed and the oil in the latter case is simply retained in the pores of the sheet.

The products, in accordance with the invention, are thus characterized by a relatively low density and high porosity. An exemplary density in accordance with the example set out hereinbefore is about 0.5 gram per cubic centimeter or a pore volume of the sheet of about 60%. Such light weight and porosity is of advantage particularly when accompanied by the flexibility of the product in the use of the material as supported absorbent pads in single or multi-ply. For example, the material may be retained by a wire mesh or the like and positioned in

proximity to the source of an oil leak, for the purpose of picking up the oil drippings, etc.

Because of the noted characteristics of strength, flexibility, good stretch properties and resistance to oil, the impregnated product is capable of use in areas commonly subject to the presence of considerable quantities of oil and may pick up two to three times its own weight of motor oil without disintegration. For example, a product in accordance with this invention might be used as a mat in a tool room or garage, or may serve as an oil resistant gasket or the like.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof.

What is claimed is:

1. An oil resistant, flexible, absorbent paper fiber product which is capable of absorbing two to three times its own weight of motor oil without disintegration comprising a paper web having a strengthening impregnant present to the extent of between about 30 to 120 parts per 100 parts by weight of fiber and which impregnant is the reaction product of an epoxy resin and a terpolymer consisting essentially of styrene-butadiene polymer having functional hydrogen wherein the styrene is present in the polymer on a dry weight basis to the extent of between about 20–40%, the component having the functional hydrogen is present to the extent of about 1–3%, and the butadiene constitutes the remainder, and the epoxy is present to the extent of between about ½ part to 5 parts per 100 parts of the styrene-butadiene impregnant also on a dry weight basis.

2. A paper product according to claim **1** wherein the impregnant is the reaction product of the polymer and between about 0.5 to 1% of epoxy on a dry weight basis.

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