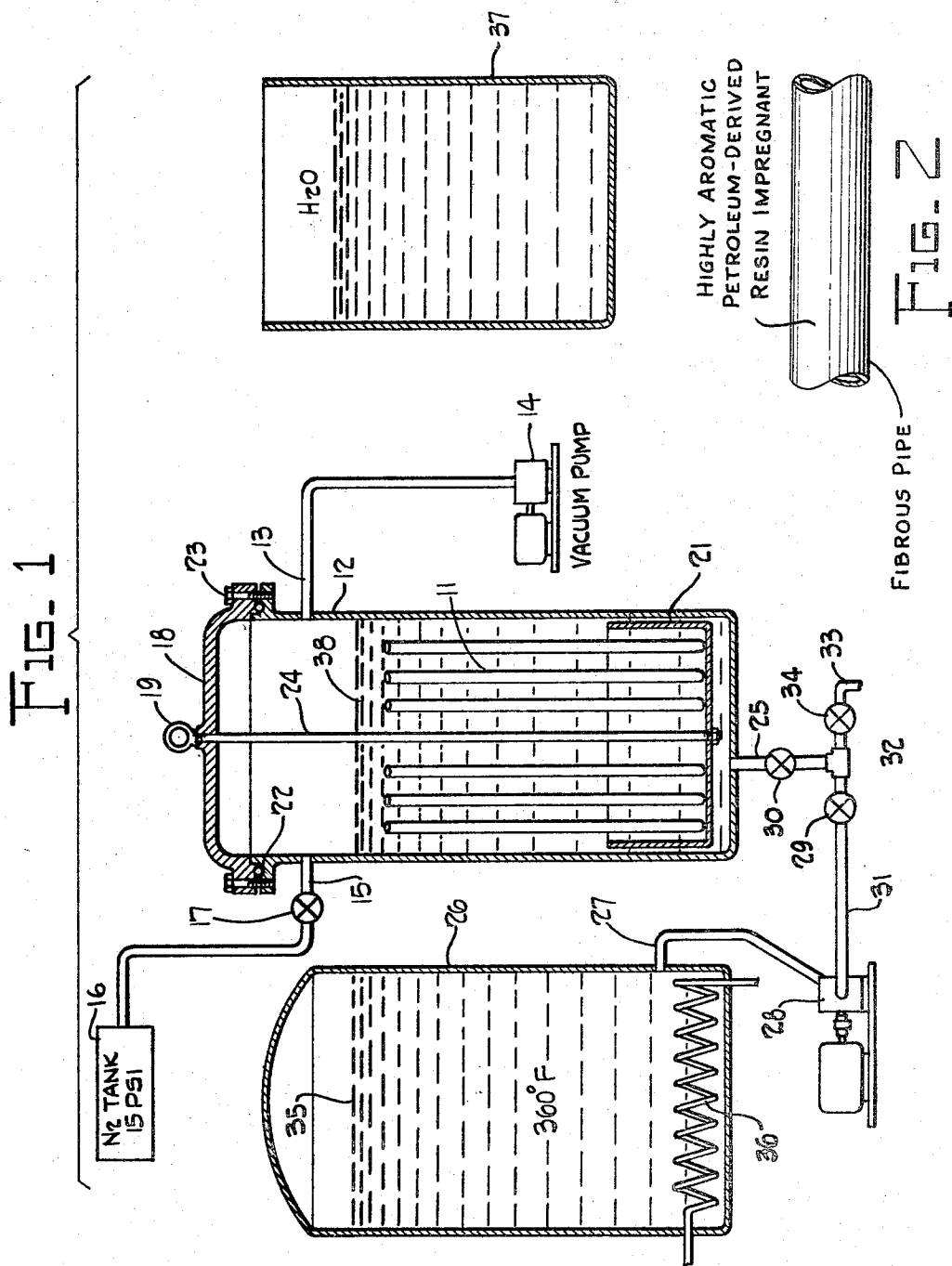


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FIBROUS PIPES IMPREGNATED WITH A HIGHLY
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3,265,093

FIBROUS PIPE IMPREGNATED WITH A HIGHLY AROMATIC PETROLEUM-DERIVED RESIN

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This invention relates to impregnated absorbent articles and more particularly to porous conduits, pipes or other tubular members, impregnated with a petroleum derived resinous material.

Tubular members of the type contemplated by this invention have for many years been utilized in underground installations as protective coverings for telephone lines and electrical cables and as conduits for drainage water, sewage and other fluids.

To survive the many adversities associated with underground installations, these tubular members must possess a variety of outstanding characteristics such as waterproofness, high crushing strength and resistance to temperature, corrosion and abrasion. Moreover, since underground installations are more or less permanent, the tubular members should retain their initial qualifications for extended periods of time.

While the prior art suggests that coal tar and petroleum derivatives may be used as porous pipe impregnants, so far as we are aware no petroleum derivative prior to our invention has enjoyed any significant degree of commercial success. Based on a recent market survey, we estimate that upwards of 90% of the bitumenized fiber pipe produced in the United States is impregnated with a coal tar derivative. The disfavor which has beset petroleum derivatives may have been due in part to the inability of pipes impregnated therewith to pass the tests established by National Bureau of Standards in Commercial Standard Publication (CS-116-54). Surprisingly, our petroleum derived impregnant passed every test and complied with every requirement set out in the above Commercial Standard.

In the annexed drawings:

FIG. 1 is a diagrammatic and schematic illustration of apparatus useful in accordance herewith.

FIG. 2 is a diagrammatic illustration of a portion of a length of fibrous pipe impregnated with a highly aromatic petroleum-derived resin in accordance with the teachings of the invention.

According to the present invention, oil permeable porous conduit members are impregnated with a petroleum derived quinoline soluble oxygenated condensation product of a distilled "clarified cycle oil" extract whereby an improved article of manufacture is obtained which is oil impermeable and which is characterized by outstanding qualifications for service in underground installations. In addition, the impregnant offers important processing and handling advantages which will be discussed in detail hereinafter.

Porous pipes and methods for their impregnation are known to the prior art and therefore will be considered only briefly here. The pipes contemplated are generally composed primarily of cellulosic fibers, but may include varying amounts of asbestos fibers, glass fibers and/or synthetic organic fibers. The pipes may be formed by a "pulp molding" process in which a slurry of fibers is filtered across a foraminous mandrel, or by forming a sheet of fibers on a Fourdrinier wire and then wrapping the sheet around a mandrel to form the tubular shape. A cellulose fiber shell may also be produced from waste paper. Porous carbon conduits may also be impregnated in accordance herewith.

Impregnation is conventionally effected in a batchwise

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operation, by placing a plurality of pipe sections in a pressure vessel; evacuating air from the vessel; introducing the impregnant, heated to a suitable degree of fluidity; and then applying either positive or negative pressure, or both in sequence, to assist the complete interstitial penetration of the impregnant. If the impregnant is sufficiently fluid, the application of pressure may not be required to effect complete impregnation.

Briefly, the impregnants of this invention are uncoked solvent extracted oxygenated condensation products of a distilled clarified cycle oil. Submission to coking temperatures increases carbonaceous insolubles or quinoline insolubles, which adversely affect impregnation. Accordingly such temperatures are avoided. Solvent extraction effects a concentration of aromatics which are desirable in the ultimate production of a highly kerosene resistant product. Solvent extraction removes non-resinous and non-condensable constituents. Distillation further concentrates the aromatics, removes non-resinous constituents and confers an increased flash point on the final product. Oxygenation of the molten material effects a condensation of aromatics effectively increasing the molecular weight of the material. The resultant product is quinoline soluble and virtually insoluble in petroleum ether (B.P. 86° F.). Flash point after distillation is a minimum of 490° F.

The petroleum-derived material constituting our impregnant is thus a distilled highly aromatic quinoline soluble fraction of petroleum oil boiling above about 600° F. and preferably within the range of 700 to 800° F., or approximately 750° F., which has been oxygenated, as by air blowing, to a Ring and Ball softening point within the range of 150° F. to 250° F. and preferably 170° F. to 180° F. A particularly suitable highly aromatic fraction is the heavy end, i.e., the second 50 vol. percent of extracted "clarified cycle oil." For purposes of this invention the term "clarified cycle oil" (also known as "decanted cycle oil") is used to describe the material obtained as bottoms in fractionating the output of a catalytic cracking process.

After the initial breakup of crude oil into raw products by simple distillation, the fraction having a boiling range of from about 500-600° F. up to about 1000-1100° F. is subjected to a catalytic cracking procedure. The output of the cracker is then fractionated into an overhead stream, one or more side streams and bottoms. Regardless of the catalyst handling system used in the cracker, appreciable quantities of powdered catalyst are carried over from the cracking unit to the fractionator and settle in the aforementioned bottoms. The bottoms are separated from the catalyst by any known clarification procedure, and recycled back to the cracking unit and subjected to further cracking. From these manipulative steps come the terms "cycle oil" and "clarified cycle oil."

More recently, new uses have been discovered for the paraffinic constituents in clarified cycle oil. These new discoveries have brought into vogue the extractive treatment of "clarified cycle oil" to separate (1), primarily the aromatics (extract) from (2), the paraffins (raffinate). We utilize the extract portion. Solvents such as furfural, phenol, B,B'-dichloro diethyl ether, nitrobenzene, Duosol (propane and cresol) and sulphur dioxide preferentially solubilize aromatics and naphthenes and may be used in the extractive treatment of clarified cycle oil. Of these, furfural is preferred for our purposes as a means for concentrating the aromatic content of the extract; i.e. to remove aliphatic and cycloaliphatic constituents.

For further details of typical procedures for the separation and extraction of cycle oil reference may be had to U.S. Patents 2,660,552 to Blanding and 2,882,220 to Mikeska et al. These patents effect the extraction of

clarified cycle oil to recover the raffinate rather than the extract, pointing up another attractive aspect of the present invention, to wit, that the improved fiber pipe impregnant can be prepared from an inexpensive, readily available material, generally considered to be of little commercial value.

Clarified cycle oil extract as defined above is a complex mixture of highly aromatic hydrocarbons and as such does not admit of absolute chemical analysis. The composition of the extract will vary as functions of the crude oil from which it is derived and the conditions of initial distillation, cracking, fractionating, etc. A typical sample of clarified cycle oil extract has been analyzed according to the Shell n-d-m procedures ("Aspects of the Constitution of Mineral Oils"; K. Van Nes et al., Elsevier Publishing Co., Inc., 1951, pp. 318-346).

as an impregnant. This product unlike other petroleum resins is characterized by the absence of carbonaceous insolubles which interfere with the impregnation. A convenient and reliable test for carbonaceous insolubles is the solubility of the impregnant in quinoline. Oxygenated condensation products of distilled clarified cycle oil extract in accordance herewith show no more than a trace of quinoline insolubles, and are preferably 100% soluble in quinoline.

For impregnation of lengths of fiber pipe 11, a tank 12 may be employed having a vacuum connection 13 to a vacuum pump 14 and a pressure connection 15 to a tank 16 of nitrogen under pressure with a shut-off valve 17 in the connection 15.

The tank 12 is provided with a removable cover 18 with a lifting eye 19 and a basket 21 for supporting the

TABLE I

Sample.....	0-10%	10-20%	20-30%	30-40%	40-50%	50-60%	60-70%	70-80%	Btms.
Grav., °API.....	11.3	5.8	3.9	2.4	0.5	-1.9	-4.5	-5.9	-14.4
d ₄ ²⁰ °C., 8 ms./cc.....	0.9574	0.9972	1.0122	1.0239	1.042	1.0591	1.0825		
Pour Point, °F.....	+25	+45	+55	+65	+70	+70	+80	+70	
Flash Point, °F.....	335	360	400	385	450	470	485	490	
Color D-155.....	2-	blue	green	2	2	2.5	4		
Vis. at 210° F. SSU.....	32.2	35.3	36.5	39.61	44.98	53.7	77.9	107.6	
Vis. at 100° F. SSU.....	48.6	80.8	105.1						
Vis. Grav. Constant.....	0.996	1.047	1.065	1.06	1.075	1.090	1.109		
n _D ²⁰ °C.....	1.5587	1.5906	1.6021	1.6141	1.6316	1.6495	1.6690		
Aniline Point, °F.....	66	69	75.5	84.5	90.5	95	92		
Total Sulphur, wt. Percent.....	1.43	2.03	2.21	1.91	1.65	1.63	1.83	1.76	1.08
Total Nitrogen, wt. Percent.....	0.025	0.05	0.062	0.067	0.054	0.047	0.062	0.063	0.055
Percent Carbon as Rings.....	67.1	66.8	66.9	63.3	61.1	58.4	57.6		
Percent Carbon as Paraffins.....	32.9	33.2	33.1	36.7	38.9	41.6	42.4		
Percent Carbon as Aromatic.....	61.3	66.8	66.9	63.3	61.1	58.4	57.6		
Percent Carbon as Naphthenes.....	5.8	0.0	0.0	0.0	0.0	0.0	0.0		
Total Rings per Molecule.....	1.94	1.97	2.05	2.09	2.1	2.04	2.07		
Rings/Mol. as Aromatics.....	1.65	1.97	2.04	2.09	2.1	2.04	2.07		
Rings/Mol. as Naphthenes.....	0.29	0.0	0.0	0.0	0.0	0.0	0.0		
Carbon Atoms/Molecule.....	15.8	17.1	17.4	17.5	19.4	19.0	20.7		
Molecular Weight.....	210	220	225	240	250	256	265	270	

Typical characteristics for the heavy ends of clarified cycle oil extract are listed below. These properties are for the heavy ends, e.g. the 40 to 100 volume percent fraction obtained by distillation to remove the light ends.

TABLE II

Gravity API.....	-8.6
Sp. gr. at 60° F.....	1.1512
Vis. SSF at 250° F.....	19.7
Flash point, °F.....	525
Ramsbottom carbon residue, wt. percent.....	14.71
Wt. percent sulfur.....	1.23
Penetration at 77° F.....	90
Ring and ball softening point, °F.....	103
ASTM distillation, °F.—vol. percent distilled, °F.:.....	
IBP.....	747
2%.....	769
5%.....	785
10%.....	800
20%.....	824
30%.....	841
40%.....	860
50%.....	887
60%.....	909
70%.....	941
80%.....	—
100%.....	—

As noted above, the heavy ends of clarified cycle oil extract, or distilled clarified cycle oil extract, are oxygenated, for example by blowing with an oxygen-containing gas, such as air, to a ring and ball softening point within the range of 150 to 250° F. and preferably 170 to 180° F. whereupon the material is then ready for use

pipe lengths 11 which are to be impregnated. Suitable sealing arrangements such as an O-ring seal 22 and hold down bolts 23 are provided. For convenience in lifting the basket 21 and the load of pipes 11 when the cover 18 is lifted, a rod 24 may be provided connecting the basket 21 to the cover 18 and the lifting eye 19.

The tank 12 is provided also with an inlet pipe connection 25 from a tank 26 containing cycle oil treated in accordance herewith having an outlet 27 connected to the impregnating tank inlet 25. A liquid transfer pump 28 may, if desired, be provided, although this will be unnecessary if the tank 12 is evacuated before the liquid is admitted thereto. Preferably a shut-off valve 30 is provided in the impregnating tank inlet 25 in order to permit evacuating the tank 12 before admitting treated cycle oil from the tank 26 when it is so desired and a shut-off valve 29 is provided in the outlet pipe 31 from the pump 28. A T-connection 32 may be provided between the valves 29 and 30 with a drain outlet 33 to a sump normally closed by a valve 34.

Suitable means are provided for heating a body of treated cycle oil 35 in the tank 26 such as steam heating coils 36, electric heaters or the like in the tank 26, or flames under the tank 26 as desired.

A water-containing quench tank 37 is provided of approximately the same size as the impregnating tank 12 and adjacent thereto so that the load 11 may be withdrawn gradually from the level of liquid 38 in the tank 12 after impregnation has been completed by removing the sealing bolts 23 and lifting the eye 19 by means of a suitable crane (not shown) and thereafter lowering the load contained in the basket 21 into the quenching tank 37.

FIG. 2, with appropriate legends, is a portion of a length of fibrous pipe impregnated with a highly aromatic

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petroleum-derived resin in accordance with the teachings of the foregoing process.

Example

A series of fibrous, tubular members of 4" nominal diameter and 12" long were placed in a pressure vessel 12. Upon sealing the vessel, a vacuum pressure of one inch of mercury absolute was applied and held for 40 minutes.

A quantity of 50 to 100 volume percent distilled clarified cycle oil extract, air blown to a ring and ball softening point of 175° F., was heated in a separate vessel to 360° F. Upon completion of the evacuation step the impregnant was introduced into the pressure vessel. A nominal positive pressure of 15 p.s.i.g. as nitrogen gas, was applied and held for 40 minutes. The pressure was then dropped, the pressure vessel opened and the impregnated tubular members slowly withdrawn from the bath of impregnant. A slow, constant rate of withdrawal is essential to insure the formation of a smooth continuous facing of impregnant on the surfaces of the pipe. This desideratum was readily effected by controlling the withdrawal rate through visual inspection. The tubular members were then quenched in water to prevent bleeding of the impregnant.

In another example, various sizes of pipe, 2", 4", 6" and 8" nominal diameter and lengths of 5, 8 and 10' were loaded together in a basket suspended in a pressure vessel and impregnated as described.

For comparative purposes this same procedure was used to impregnate fibrous tubular members with a coal tar derivative, supplied by a local bitumenized fiber pipe manufacturer. The properties of our impregnant and the commercially successful coal tar derivative were compared as follows:

TABLE III

	Coal Tar Derivative	Air Blown Distilled Clarified Cycle Oil Extract, 50 to 100 Vol. Percent
Specific Gravity (60° F.)	1.252	1.190
Ring & Ball Softening Point (° F.)	172	168
Saybolt Furol Viscosity (Secs.) at:		
310° F.	37.0	53.0
325° F.	19.0	32.9
350° F.	12.0	21.0
Flash Point (° F.)	460	515
Quinoline Solubility at 75° F., percent	97	100

The advantages of our petroleum derivative in comparison with coal tar impregnants presently enjoying wide commercial use, include the following:

(1) The supply of impregnant is stable being tied to the stable petroleum industry, instead of being tied to steel production, which is variable.

(2) Impregnant may be compatibly admixed with conventional impregnants, e.g. coal tar impregnants.

(3) Absence of phenolic or other harmful vapors avoids physiological effects of phenolics and health hazards in processing, and enables pipe to be installed in hot, humid days without burning hands.

(4) At impregnation temperatures, no insolubles, good impregnation, smooth inside surface of pipes, avoiding poor flow co-efficient for the pipe and avoiding formation of lumps which may collect solid compounds of sewage and eventually lead to clogging the pipe.

(5) Low volatility increases the effective vacuum available during impregnation.

(6) Impregnation increases weight of pipe less than with impregnant previously available.

(7) Low water absorbtivity of pipe.

(8) Negligible kerosene solubility of pipe under conditions of use.

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(9) High beam strength of pipe.

(10) High crushing strength of pipe.

(11) Pipe resistant to sulfuric acid, sodium carbonate, sodium sulfate and boiling water.

(12) Pipe does not flatten or exude pitch when maintained at an elevated temperature.

(13) High flash point of impregnant offers a large margin of safety in impregnation process.

(14) Less volatile materials in the impregnant.

(15) Pipe resistant to cold flow.

While the invention has been described as embodied in concrete form and as operating in a specific manner in accordance with the provisions of the patent statutes, it should be understood that the invention is not limited thereto, since various modifications will suggest themselves to those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. A conduit comprising in combination an oil permeable wall and an impregnant having a ring and ball softening point within the range of 150 to 250° F. consisting essentially of a highly aromatic, quinoline soluble oxygenated condensation product of a distilled cycle oil extracted with an extractant selected from the group consisting of furfural, phenol, B,B'-dichloro diethyl ether, nitrobenzene, and sulphur dioxide, impregnated therein and coacting therewith to render said wall oil impermeable.

2. A conduit in accordance with claim 1 in which the oil permeable wall comprises cellulose fiber.

3. A conduit in accordance with claim 1 in which the oil permeable wall is a tubular paper wall.

4. An oil impermeable body comprising in combination an oil permeable wall and an impregnant having a ring and ball softening point within the range of 150 to 250° F. consisting essentially of a highly aromatic, quinoline soluble oxygenated condensation product of a distilled cycle oil extracted with an extractant selected from the group consisting of furfural, phenol, B,B'-dichloro diethyl ether, nitrobenzene, and sulphur dioxide, impregnated therein and coacting therewith to render said wall oil impermeable, said body having mechanical strength, chemical resistance, low absorptivity and smooth surface properties.

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