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(54) Collector membrane.

(57) A silicone membrane collector is disclosed which is formed of room temperature vulcanizing rubber. The silicone membrane receives or collects, by intimate contact, a thermoplastic pressure-sensitive ink formulation in the form of one or more portions of a design. The design thus collected may be deposited onto another surface by intimate mechanical contact of the membrane therewith. The membrane may be between 0.2" (5.08 mm) and 0.02" (0.508 mm) thick, and may be formulated to have a tensile strength of at least 50 psi (3.45 bars), an elongation of at least 150% and a surface tack of between 20 and 1200 g.

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COLLECTOR MEMBRANE

This invention relates to a collector membrane.

A printing apparatus for decorating ware is disclosed in European Patent Specification 0082693 and a European Patent Application filed by us and claiming priority from U.S. Patent Application Serial No. 419,471, filed 17th September, 1982. The apparatus includes a flexible membrane collector. Pressure-sensitive, thermoplastic inks, especially useful with such a device, are disclosed in copending European Patent Application No. 82306905.9.

The present invention discloses a collector membrane having properties most preferred for quality print results.

The present application discloses a silicone membrane collector formed of room temperature vulcanizing rubber. The silicone membrane receives or collects, by intimate contact, a thermoplastic pressure-sensitive ink formulation in the form of one or more portions of a design. The design thus collected may be deposited onto another surface by intimate mechanical contact of the membrane therewith. The membrane may be between 0.2" (5.08mm) and 0.02" (0.508 mm) thick, and may be formulated to have a tensile strength of at least 50 psi (3.45 bars), an elongation of at least 150% and a surface tack of between 20 and 1200g.

The present invention utilizes room temperature vulcanizing (RTV) silicones for a collector membrane. Such materials are generally divided into two classifications, each based upon a particular curing mechanism of the material. For example, materials known as addition-cure silicones contain silicone hydride cross-linkers which react with vinyl groups when mixed therewith. A platinum compound is used as a catalyst. There are no volatile by-products that are produced during the curing step. The curing proceeds evenly in deep sections and is heat acceleratable.

Another type, known as condensation-cure silicones, has a condensation reaction in which an alkoxy cross-linker reacts with a silanol group in the presence of a stanous soap as the catalyst. A volatile alcohol by-product evaporates as the reaction proceeds.

It is not entirely understood how the composition, the curing mechanism, the fillers and the degree of cross-linking affect the surface energy and surface tack. The surface energy and tack dictate the release properties of a silicone material. The condensation-cure silicones are often more releasing, because they generally appear to have a lower surface tack. Consequently, they are often used as the first transfer surface or offset surface in a multiple surface system. On the other hand, the addition-cure silicones are often less releasing and are generally used as the second transfer surface, i.e. a collector. The first surface picks up ink from a heated gravure plate for transfer to the second transfer surface or collector. Formulation parameters other than the curing mechanism also have significant affects on the release properties, and thus condensation and addition types have overlapping characteristics.

It is known that any given silicone formulation may be made more releasing by adding dimethyl siloxane oil. Although the viscosity, as determined by molecular weight of the oil, is relatively unimportant, the higher viscosity oils are usually avoided because they cause the surface of the silicone to become greasy, and therefore susceptible to contamination. The release properties increase, that is the surface energy decreases, as the amount of oil is increased. A preferred viscosity range for the oil is between about 20 and 1000 centistokes.

At very high oil levels, the affect on durometer, which decreases with increasing oil content, may cancel any further improvement in the release characteristic of the material. Extreme values of durometer interfere with obtaining a favourable release. A high durometer silicone does not conform well to surfaces being printed, whereas a low durometer silicone makes it difficult to exert a sufficient transfer pressure. For those reasons, durometer is generally kept within a range of from about 30-90 points, as measured on a Shore-OO durometer gauge, manufactured by Shore Instrument and Manufacturing Company. The most convenient or preferred working range of durometer is from 50-75 points. For a collector membrane, the oil may comprise from about 0 to 50% of the silicone formulation. A preferred oil content for a typical membrane formulated from Dow Corning Silastic L is between about 30 and 50 parts by weight. Table I shows that increasing the oil content of the silicone reduces the tack and durometer characteristics of Silastic L. In a prepared embodiment, 40 phr is added to the silicone (two Shore readings are given).

Table I

Oil Addition (phr)*	Tack (grams)	Durometer Shore-A	Durometer Shore-OO
0	579	35	78
20	338		
40	250	10	62
60	207		
80	164		

*phr - parts by weight addition per hundred parts base resin.

The membrane described herein may be prepared by injecting or pouring liquid unvulcanized material into a polished metal mould at room temperature. Thereafter, the material is allowed to cure at room temperature or is heat accelerated by curing in an oven at a temperature up to about

200°F (93°C) to form a cohesive body between about 0.02" (0.508 mm) and 0.20" (5.08 mm) thick. The material may be directly cast over the support frame, primed with 1200 Dow Corning primer, or it may be removed from the mould and either bonded to a support frame (not shown herein, but see European Patent Specification 0082693 referred to above) with a silicone adhesive, such as General Electric RTV-700, or mechanically attached to such support frame. The support frame is generally a metal material with a centrally located circular hole from 3" (76.2 mm) to 24" (609.6 mm) in diameter. The membrane is mounted or moulded to cover this circular hole. Upon attachment to the frame, the membrane may be stretched up to about 25% of its original size.

In the collector printing process, the membrane is held by a vacuum against a support or backing member when printed upon by a series of offset printing stations. After the print is completely formed upon the collector membrane surface, the support is removed, and a silicone pad moves through the hole in the support frame against the back (unprinted) side of the membrane, urging the membrane against the ware surface to be decorated. The decoration transfers from the membrane to the ware surface upon contact therewith.

The membrane thickness should be between about 0.020" (0.508 mm) and 0.200" (5.08 mm). The lower limit is the minimum thickness providing minimum acceptable mechanical strength. The upper limit is the maximum thickness providing minimum acceptable shape conformity. For example, intimate contact is required for total transfer from the membrane to the ware. In the case of ware shapes which have relatively abrupt contour changes, a membrane with a thickness beyond 0.200" (5.08 mm) would be too stiff to be conformed in a manner to prevent air from being trapped between the membrane and the ware (see European Patent Specification 0082693 referred to above). The trapped air would then prevent the intimate contact. A preferred thickness range for membrane would be between 0.030" (0.762 mm) and 0.090" (2.29 mm).

The tensile strength and the elongation are measured in accordance with ASTM D-412. The preferred minimum values for tensile strength and elongation are 50 psi (3.45 bars) and 150%, respectively.

The most important property of a silicone membrane collector is its release characteristic. To function as both a receptor for ink and a donor of the same, the collector membrane must have a release characteristic within a certain range. Numerous attempts have been made to quantify such a property. Most attempts have not been found to be sensitive enough to differentiate between numerous transfer silicones. A test has been found for quantifying the surface release characteristics of RTV silicones as illustrated in the attached Tables II and III. The preferred equipment for the test is a model 80-2 Polyken Probe Tack Tester, manufactured by Testing Machines Inc. Amityville, New York. The test results in a probe tack reading which measures the force necessary to separate a metal probe from contact with the silicone surface. There is good correlation between the test and observed release characteristics. The test is far less influenced by the silicone durometer than other tests. In general the higher the tack value, the more affinity the silicone exhibits for pressure-sensitive inks of the type discussed in U.S.S.N. 419,196. Table II summarizes test parameters.

TABLE II

PARAMETERS OF POLYKEN PROBE TACK TEST FOR MEASUREMENT OF SILICONE SURFACE TACK*

Parameter	Setting
Dwell Time	1 sec
Separation Speed	1 cm/sec
Probe Surface Area	0.196 cm^2
Temperature	20 °C
Relative Humidity	40%
Load	1010 gm/cm^{2}**

*Tack is reported as average of 10 readings on 3 samples. Samples are conditioned, after curing, in an environmentally controlled room for 24 hours prior to testing.

** 1050 gm/cm^2 including sample and sample holder weight.

This test has demonstrated its accuracy, in that many known silicone materials have been rated in the correct release order. Such correct order has been demonstrated through actual printing practices. For example, it is known that in order for an ink to transfer from one surface to another, the release characteristic of an ink carrying member must be greater than the same characteristic of the next surface against which the ink and the transfer member must be urged. In the past, the ease of release has been theorized to increase with decreasing surface energy. However, all silicones have relatively low surface energies, and among various silicones the ease of release has been found to correlate with surface tack measurements. Successive transfer from one surface to another is described in the aforementioned U.S. Patent Applications. Table III summarizes the characteristics of commerical RTV silicones:

TABLE III

CHARACTERISTICS OF COMMERCIAL RTV SILICONES

Category of Release	Silicone[1]	Cure[2]	S.G.[3]	Durometer Shore A
High	DC 3110	C	1.17	44
	GE RTV 602	C	1.00	23
	GE RTV 11	C	1.18	45
	SWS V-54	C	1.18	45
Moderately High	RTV 511	C	1.20	43
	SWS 04478	C	1.14	25
	GE RTV 700	C	1.06	31
	GE RTV 41	C	1.31	43

TABLE III (contd.)

Category of Release	Silicone[1]	Cure[2]	S.G.[3]	Durometer Shore A
	SWS 833	C	1.51	40
Moderately Low	Silastic E	A	1.12	42
	GE RTV 615	A	1.01	37
Low	Silastic L	A	1.29	36
	Silastic J	A	1.29	50
	GE RTV 630	A	1.28	63

Category of Release	Silicone	% Rebound	Tack[4]	Tear Strength (psi)	Tear Strength (bars)
High	DC 3110	68	124	20	1.38
	GE RTV 602	70	62	10	0.69
	GE RTV 11	74	83	15	1.03
	SWS V-54	68	102	18	1.24
Moderately High	RTV 511	67	143	25	1.72
	SWS 04478	52	159	90	6.21
	GE RTV 700	50	187	125	8.62
	GE RTV 41	73	172	30	2.07
	SWS 833	68	170	40	2.76
Moderately Low	Silastic E	60	312	90	6.21
	GE RTV 615	57	444	25	1.72
Low	Silastic L	44	579	65	4.48
	Silastic J	50	514	70	4.83
	GE RTV 630	46	537	85	5.86

TABLE III (contd.)

Category of Release	Silicone	Tensile Strength (psi)	(bars)	% Elongation
High	DC 3110	330	22.8	150
	GE RTV 602	100	6.9	200
	GE RTV 11	350	24.1	180
	SWS V-54	400	27.6	155
Moderately High	RTV 511	350	24.1	180
	SWS 04478	650	44.8	275
	GE RTV 700	600	41.4	400
	GE RTV 41	500	34.5	200
	SWS 833	800	55.2	130
Moderately Low	Silastic E	700	48.3	400
	GE RTV 615	900	62.1	150
Low	Silastic L	550	37.9	350
	Silastic J	750	51.7	175
	GE RTV 630	800	55.2	420

[1] DC - Dow Corning Corp., Michland, MI
SWS - SWS Silicone Corp., Adrian, MI
GE - General Electric Co., Waterford, NY

[2] C - Condensation Cure
A - Addition Cure

[3] S.G.- Specific Gravity

[4] In grams as measured on a Polyken probe tack tester; 1010 g/cm^2, 1 sec. dwell, separation speed 1 cm/sec, 20°C, 40-50% relative humidity.

For a collector silicone to properly function in a double offset (collector) process, it must exhibit intermediate ink affinity between the first offset silicone surface, and the ware or substrate surface being printed. Generally, silicones have good release characteristics and exhibit low affinities for most inks. A collector silicone, however, must be chosen to exhibit greater affinity for an ink than the first offset silicone printing onto the collector. In terms of the test, herein described, this means that the collector silicone must be chosen with a higher tack than the silicone used for the first offset surface, otherwise transfer onto the collector cannot occur.

The above is true for all inks. However, the absolute value of the required tack difference between the first offset surface and the collector, for consistent transfer between surfaces, is dependent upon the chemical nature of the particular ink employed. Some inks can transfer effectively between surfaces with a relatively small tack difference. Other inks may require a higher tack difference to achieve consistent 100% ink transfer. In no case, however, will a silicone, of a selected tack transfer an ink to another silicone of a lower tack.

In actual process operation, the surface tack of a silicone increases, or its release characteristic decreases, with repeated release cycling. Eventually, the silicone deteriorates to the point where complete transfer is not obtained, therefore, the process is no longer operable. At this point, the silicone surface must be replaced.

CLAIMS:

1. A collector membrane comprising a material formed of room temperature vulcanizing silicone material, said membrane serving to receive thereon by intimate contact a thermoplastic, pressure-sensitive ink formulation in the form of a design by intimate contact with a surface carrying said design, the membrane serving to deposit the design onto another surface by intimate mechanical contact therewith, the membrane being between 0.02" (0.508 mm) and 0.2" (5.08 mm) thick and being formulated from a silicone material exhibiting a release characteristic between 20 and 1200 g from a probe loaded against the material at about 1050 g/cm^2, the probe having a surface area of about 0.196 cm^2; a dwell time of about 1 sec, a separation speed of about 1 cm/sec, at a temperature of about 20°C and a relative humidity of about 40%.

2. A silicone membrane as claimed in claim 1, wherein the material has a hardness of about 50 to 75 points as measured on a Shore-00 durometer gauge.

3. A silicone membrane as claimed in claim 1 or 2, wherein the silicone material includes dimethyl siloxane oil in an amount up to about 50% of the silicone formulation.

4. A silicone membrane as claimed in claim 3, wherein the silicone is Dow Corning Silastic L containing from about 30 to about 50 parts per weight of said oil.

5. A silicone membrane as claimed in claim 4, wherein said oil has a viscosity of from 20 to 1000 centistokes.

6. A silicone membrane as claimed in any preceding claim, wherein the membrane is between about 0.030" (0.762 mm) and about 0.090" (2.29 mm) in thickness.

7. A silicone membrane as claimed in claim 6, wherein said membrane is stretched up to about 25%.

8. A silicone membrane as claimed in any preceding claim, wherein the silicone material is formulated to have a tensile strength of at least 50 psi (3.45 bars) and an elongation of at least 150%, measured in accordance with ASTM D-412.