

(11) (21) (C) **2,073,253**  
(86) 1991/09/11  
(87) 1992/05/22  
(45) 2000/03/28

(72) Lewis, Thomas E., US

(72) Nowak, Michael T., US

(73) Presstek, Inc., US

(51) Int.Cl.<sup>5</sup> C08L 83/04, G03F 7/075, C09D 183/04

(30) 1990/11/21 (616,377) US

(54) **FORMULATIONS DE REVETEMENT AU SILICONE ET  
PLAQUES PLANOGRAPHIQUES CONSTITUEES DE  
CELLES-CI**

(54) **SILICONE COATING FORMULATIONS AND PLANOGRAPHIC  
PRINTING PLATES MADE THEREWITH**

(57) Formulations de silicone à deux constituants comprenant un composant de silicone à poids moléculaire élevé et un polymère de silicone de faible poids moléculaire. Les constituants sont mélangés dans des proportions variables avec un agent de réticulation pour produire des compositions de viscosités et de dispersibilités variables. Le constituant de poids moléculaire élevé est un composé de polysiloxane linéaire possédant un poids moléculaire d'au moins 300,000, et de préférence de 500,000 ou plus. Le constituant de faible poids moléculaire possède une structure similaire, avec un poids moléculaire qui n'est pas supérieur à 70,000. On procède à diverses substitutions pour faciliter la réticulation entre les constituants. Les formulations conviennent bien à des applications de revêtements, et peuvent être employées utilement en tant que revêtements pour des plaques planographiques.

(57) Two-component silicone formulations consisting of a high-molecular-weight silicone component and a low-molecular-weight silicone polymer. The components are combined in varying proportions with a cross-linking agent to produce compositions of varying viscosities and dispersibilities. The high-molecular-weight component is linear polysiloxane compound with a molecular weight of at least 300,000, and preferably 500,000 or higher. The low-molecular-weight component has a similar structure, with a molecular weight no greater than 70,000. Various substitutions are made to facilitate cross-linking among components. The formulations are well-suited to coating applications, and can advantageously be used as coatings for planographic plates.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08L 83/04, G03F 7/075</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/09659</b> <b>(43) International Publication Date:</b> 11 June 1992 (11.06.92)
<b>(21) International Application Number:</b> PCT/US91/06551 <b>(22) International Filing Date:</b> 11 September 1991 (11.09.91) <b>(30) Priority data:</b> 616,377 21 November 1990 (21.11.90) US <b>(71) Applicant:</b> PRESSTEK, INC. [US/US]; 8 Commercial Street, Hudson, NH 03051 (US). <b>(72) Inventors:</b> LEWIS, Thomas, E. ; 27 Pilgrim Circle, E. Hampstead, NH 03826 (US). NOWAK, Michael, T. ; 38 Meadowbrook Lane, Gardner, MA 01440 (US). <b>(74) Agents:</b> CESARI, Robert, A. et al.; Cesari and McKenna, 30 Rows Wharf, Boston, MA 02110 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>  <div style="text-align: center; font-size: 1.5em; font-weight: bold;">2073253</div>
<b>(54) Title:</b> SILICONE COATING FORMULATIONS AND PLANOGRAPHIC PRINTING PLATES MADE THEREWITH  <b>(57) Abstract</b>  Two-component silicone formulations consisting of a high-molecular-weight silicone component and a low-molecular-weight silicone polymer. The components are combined in varying proportions with a cross-linking agent to produce compositions of varying viscosities and dispersibilities. The high-molecular-weight component is linear polysiloxane compound with a molecular weight of at least 300,000, and preferably 500,000 or higher. The low-molecular-weight component has a similar structure, with a molecular weight no greater than 70,000. Various substitutions are made to facilitate cross-linking among components. The formulations are well-suited to coating applications, and can advantageously be used as coatings for planographic plates.		

1

SILICONE COATING FORMULATIONS  
AND PLANOGRAPHIC PRINTING  
PLATES MADE THEREWITH

2073253

**I. Background of the Invention**

**A. Field of the Invention**

The present invention relates to polymeric silicone formulations, and in particular to coating formulations useful for lithographic and other planographic printing plate constructions.

**B. Description of the Related Art**

Polyorganosiloxane compounds, or "silicones", can be synthesized in a wide variety of forms, and are utilized in numerous commercial applications. Silicone compounds are based on the repeating diorganosiloxane unit  $(R_2SiO)_n$ , where R is an organic radical and n denotes the number of units in the polymer chain. Each end of the linear chain is terminated with a functional or non-functional end group; the chain may also be "branched" so as to deviate from a strictly linear structure.

The physical properties of a particular silicone formulation depend on the length of the polymer chain, the nature of the organic functional groups bonded to the silicon atoms, and the terminal groups (more precisely, the alpha and omega groups) at each end of the chain. For example, the most common silicone compounds are based on the polydimethylsiloxane unit,  $-Si(CH_3)_2O-$ , which, due to the relatively small organic content of the chains, have a limited range of compatibility with organic compounds. By contrast, silicones containing aryl functional groups tend to exhibit properties more commonly



2073253

-2-

associated with organic materials, and such silicones are generally miscible with a broader range of such materials.

Many long-chain silicone compounds exhibit rubber-like characteristics. These compounds are employed in numerous industrial and commercial environments as a direct substitute for natural rubber. "Silicone rubber" is typically prepared from "silicone gum", which connotes a viscous, high-molecular-weight polydiorganosiloxane compound, by cross-linking (or "curing") the polymer chains. Curing promotes the elasticity commonly associated with rubber materials and, because it largely eliminates gross molecular movement, also increases viscosity dramatically.

Curing can be accomplished in a number of ways, but generally depends on the presence of reactive functional groups on the polymer chains that interact and bond with one another. "Condensation cure" reactions refer to those in which a small molecule is eliminated when the two functional groups are joined. Typical condensation-cure reactions in silicone chemistry involve reaction of silanol functional groups with other such groups to produce an oxygen linkage with the elimination of water. "Addition cure" reactions involve no loss of species, and can involve, for example, hydrosilylation reactions between olefinic functional groups (such as vinyl) and hydrosiloxane groups.

Variations on the traditional condensation-cure reaction include the "moisture-cure" approach, in which a precursor functional group is first hydrolyzed to form the reactive silanol group, which then combines with another silanol group as discussed above. Suitable precursor compounds include acetoxo, alkoxy and ketoxime functional silanes, which form acid, alcohol and ketoxime byproducts, respectively, upon hydrolysis.

-3-

Silanol-functional silicones and mixtures of silanol-functional silicones with silicones containing acetoxy, alkoxy or ketoxime groups are relatively stable so long as moisture is excluded; this is particularly true for silicone polymers having appreciable molecular weights. Obtaining useful reaction rates generally requires a catalyst such as a metal carboxylate compound.

Silanol groups also react with hydrosiloxane species to liberate hydrogen and produce the silicon-oxygen-silicon linkage characteristic of the condensation cures. This reaction also requires use of a metal salt catalyst (such as dibutyltin diacetate) to achieve useful reaction rates. Because this reaction proceeds rapidly when catalyzed, it is widely used for silicone coating formulations applied on a coating line to a web substrate.

In addition to these mechanisms, silicone polymers are sometimes cross-linked using multifunctional acrylate or methacrylate monomers. The polymers are exposed to an electron beam or combined with a photoinitiator species and then exposed to actinic radiation in order to produce free-radical derivatives that combine with one another. Other approaches to cross-linking are described in U.S. Patent No. 4,179,295.

The reactive, cross-linking functional groups can be incorporated at the termini of a polymer chain, or at a desired frequency within a copolymer chain. In order to achieve the elastomeric properties associated with silicone rubber, large polymeric units ("base polymers") are cross-linked by smaller

-3a-

oligomers or multifunctional monomers. Frequently, this is accomplished by providing the base polymers with one type of functional group, and incorporating the complementary



-4-

functional group on the cross-linking molecules. For example, the addition-cure reaction described above can be utilized to produce elastomeric compositions by combining base polymer or copolymer chains that contain olefinic functional groups with small cross-linking molecules that have hydrosiloxane functional termini.

Silicone rubber coatings have been adopted by some manufacturers of planographic printing plates. Planographic printing, as contrasted with letter-press and gravure printing, relies on plate constructions in which image and non-image areas lie substantially in the same plane. The plate is prepared by altering the affinities of different areas of the plate for ink. Depending on the type of plate imaging system employed, non-image plate areas become (or remain) oleophobic, or ink-repellent, while image areas remain (or become) oleophilic, or ink-accepting. Ink applied to the plate surface, e.g., by a roller, will adhere to the oleophilic image areas but not the oleophobic non-image areas. The inked plate is then applied to the recording medium (in direct printing) or to an intermediate "blanket" cylinder which then transfers the image to the recording medium (in offset printing).

Manufacturers of planographic printing plates often employ silicone rubber compositions as plate coatings due to their oleophobic character, which provides compatibility with conventional planographic printing techniques. Silicone coatings are commonly used in conjunction with so-called "dry" plates. In contrast to the traditional "wet" plate, which requires application of a fountain or dampening solution to the plate prior to inking in order to prevent ink from adhering to and transferring from non-image areas, the non-image material of dry plates is itself sufficiently ink-repellent that no fountain solution is necessary.

One hypothesis explains this effect as arising from interaction between the non-image component of a dry plate and the (usually aliphatic) solvent or solvents employed in printing inks, resulting in the formation of a thin layer of solvent on the surface of the non-image component. Like the fountain solution of a wet plate, this surface layer acts as a boundary and prevents the ink from adhering to the plate.

Blank dry plates are subjected to an imaging process that removes the silicone coating from image areas to reveal an oleophilic surface. Imaging can be accomplished in a number of ways. Photosensitization methods rely on incorporation of a photoresist material in the plate structure which, upon exposure to radiation (e.g., visible light), alters the solubility or anchorage properties of the silicone. For example, in typical commercial plates, exposure to light can result either in firm anchorage of the silicone coating to the plate (in positive-working plates) or destruction of the existing anchorage (in negative-working plates). Depending on the process chosen, the plate is first exposed to actinic radiation passing through a positive or negative rendition of the desired image that selectively blocks transmission of the radiation to the plate. After this exposure step, the plate is developed in chemical solvents that either anchor the exposed silicone or remove it to produce the final, imaged plate.

For example, a number of photosensitive dry-plate constructions are currently known and used in the art. In one approach, the photosensitive material is combined with the silicone coating prior to its application onto a substrate. Another construction relies on incorporation of the photosensitive compound within an underlying layer, exposure either weakening or strengthening the bond between layers. See, e.g., U.S. Patent Nos. 3,511,178 and 4,259,905. In a third alternative, ink-accepting toner particles are fixed to



-6-

the silicone surface according to the desired image pattern.

Plates can also be imaged by means other than photoexposure, e.g., using spark-discharge apparatus (such as that described in U.S. Patent No. 4,911,075, that utilize electronic signals to locate and produce a spark at the precise positions on the plate where the silicone coating is to be removed to reveal an underlying oleophilic surface. The spark-discharge apparatus can make contact with the plate or be held at a relatively fixed distance above the plate during the imaging process.

Silicone compositions used as coatings for planographic printing plates typically include two basic constituents, namely, a primary polyorganosiloxane base-polymer component and a smaller cross-linking component. The base component is usually a linear, predominantly polydimethylsiloxane copolymer or terpolymer containing unsaturated groups (e.g., vinyl) or silanol groups as reactive centers for bonding with the cross-linking molecules. These groups are commonly situated at the chain termini; alternatively, it is possible to utilize a copolymer incorporating the reactive groups within the chain, or branched structures terminating with the reactive groups. It is also possible to combine linear difunctional polymers with copolymers and/or branch polymers. **See, e.g.,** published Japanese Patent Applications 1-118843 and 1-179047.

The cross-linking component is generally a multifunctional, monomeric or oligomeric compound of low molecular weight, which is reacted with the first component to create connections among the chains thereof. The curing

-6a-

reaction generally requires some type of catalyst, either chemical or physical, to produce favorable kinetics. Platinum metal complexes (such as chloroplatinic acid) are often

employed to facilitate addition cures, while metal salt catalysts (such as a dialkyltin dicarboxylate) are frequently used in conjunction with condensation cures.

If the functional groups of the cross-linking component are situated at the chain termini, cross-linking molecules will form bridges among the base-polymer molecules (particularly if the latter have functional groups distributed along the chains). On the other hand, if the cross-linking component contains functional groups distributed along its length, each molecule will form numerous points of attachment with the base-polymer molecules. Typically, this type of cross-linking molecule is combined with base polymers having chain-terminal functional groups in order to maximize the number of different base-polymer molecules attached to each cross-linking chain.

Modifiers can be added to alter physical properties, such as adhesion or rheology, of the finished coating. One can also add colorants, in the form of dyes or pigments, to the silicone formulation to facilitate quality-assurance evaluation or monitoring of the photoexposure process. Pigments can also be used to enhance imaging performance in plates that will be imaged using non-contact spark discharge apparatus, as described in U.S. Patent No. 5,109,771.

Current silicone coating formulations suffer from a number of disadvantages, some stemming from physical characteristics of the polymer system itself, and others arising from the requirements of available coating apparatus. Silicone coatings are generally prepared by combining a silicone polymer with a solvent (usually aliphatic) and, possibly, other volatile components to control viscosity and assist in deposition. Because the solvent evaporates after the



2073253

-8-

coating is applied, the amount of silicone actually deposited per unit surface area depends on the relative proportions of silicone and volatile components; this proportion is referred to as the "solids content" of the composition, and is typically expressed as a percentage. Too little solvent can produce a coating that is difficult to apply, while excessive proportions of solvent can result in deposition of too little of the actual silicone material during coating, thereby reducing plate durability. The relatively low-weight polymers currently employed for producing printing plates tend to exhibit low solution viscosities; because of the necessity of preserving a minimum viscosity level for coating purposes, this characteristic limits the extent to which low-weight silicones can be diluted with solvent to control the deposition rate. Furthermore, these coatings also tend to require a narrow range of solids content for uniform application, a constraint that results in further limitation of the ability to vary dilution.

Finally, low-weight silicone compositions form poor dispersions with solid particles. For a growing number of platemaking applications, introduction of pigments or other particles is necessary for optimum plate performance. Not only is it difficult initially to disperse particles in low-weight silicones, but over time the particles that have, in fact, been dispersed tend to reagglomerate. Moreover, the above-noted problems involving low solution viscosities and narrow solids-content requirements become accentuated when particles are introduced into low-weight compositions.

A silicone coating composition is applied to a plate substrate using any of a variety of well-known coating techniques. The choice of technique is critical not only to the ultimate performance of the plate, but also to the efficiency and reliability of the overall platemaking process. Typical coating techniques include roll coating, reverse-roll

-9-

coating, gravure coating, offset-gravure coating, and wire-wound rod coating. The coating procedure must be rapid enough to achieve a satisfactory production rate, yet produce a highly uniform, smooth, level coating on the plate. Even small deviations in coating uniformity can adversely affect plate performance, since the planographic printing process depends strongly on coplanarity of image and non-image areas; in other words, the printing pattern reproduced by the plate must reflect the configuration of oleophilic and oleophobic areas impressed thereon, and remain uninfluenced by topological characteristics of the plate surface.

Because the physical properties of a given silicone formulation can be varied only to a limited extent by the use of solvents and modifiers (especially in the case of low-weight silicones), particular coating formulations tend to favor use in conjunction with a particular type of coating line. For example, addition-cure coatings having 100% solids content are most advantageously applied using offset gravure-type coating equipment. For formulations having low viscosities (which typically imply low solids contents), roll-coating and rod-coating applications are preferred.

However, as a practical matter, the number of coating lines available to a particular manufacturer is likely to be limited. It may therefore prove impossible to utilize a particular silicone formulation with readily available coating technology, forcing plate manufacturers to choose formulations based on compatibility with their coating lines rather than optimal performance for a given application.

This limitation can prove appreciable, since coating properties required for a particular application may narrow the range of acceptable formulations. Some coating properties, such as durability, can depend not only on the silicone



2073253

-10-

formulation or solids content, but also on the surface to which the coating is applied and the environment in which it is used. Other characteristics, such as the ability of the silicone matrix to accept and retain dispersions of large amounts of particulate material (a particularly important feature for spark-discharge planographic applications), can rule out entire classes of formulations and/or severely limit the number of coating techniques that may be employed.

## II. Description of the Invention

### A. Objects of the Invention

It is, therefore, an object of the present invention to provide novel silicone formulations containing two base polymers, the proportions of which can be varied to control the viscosity of the coating composition and the physical properties of the cured coating.

It is another object of the present invention to provide silicone formulations into which relatively large amounts of particulate material can be readily dispersed and maintained as a stable dispersion.

It is a further object of the invention to provide silicone formulations that may be uniformly applied to a planographic printing plate with good control of the amount of coating actually deposited on a surface.

Other objects will, in part, be obvious and will, in part, appear hereinafter. The invention accordingly comprises the compositions, features of construction, combination of elements, arrangement of parts, and relations of process steps that will be exemplified in the following description, and the scope of the invention will be indicated in the claims.



## B. Summary of the Invention

The compositions of the present invention comprise silicone systems having two primary components, a high-molecular-weight silicone gum and a distinctly lower-molecular-weight silicone polymer. These components are combined in varying proportions with a suitable cross-linking agent to produce compositions of varying viscosities, and good dispersibilities and dispersion stability.

10 According to one aspect of the present invention there is provided a polymeric silicone composition comprising:

a. a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain;

b. a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one  
20 functional group; and

c. a cross-linking component having functional groups complementary to those of the first and second polysiloxane components.

According to a further aspect of the present invention there is provided a method of preparing a coating composition, the method comprising the steps of:

11a

- a. combining, to form a mixture, a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain; a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one functional group; and a cross-linking component having functional groups complementary to those of the first and second polysiloxane components;
- b. combining the mixture with a solvent; and
- c. curing the mixture.

According to another aspect of the present invention there is provided a planographic printing plate capable of being imaged, comprising a substrate having applied to at least one surface thereof a polymeric silicone composition which itself comprises:

- a. a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain;
- b. a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units

11b

capped by terminal siloxane units containing at least one functional group; and

c. a cross-linking component having functional groups complementary to those of the first and second polysiloxane components.

According to a still further aspect of the present invention there is provided a method of preparing a planographic plate comprising coating at least one surface of a substrate with a polymeric silicone composition which itself comprises:

a. a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain;

b. a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one functional group; and

c. a cross-linking component having functional groups complementary to those of the first and second polysiloxane components.

As used herein, the term "base polymer component" refers to one of the primary polymers. The fact that we describe compositions having more than one base polymer component should not lead to confusion with descriptions of



traditional silicone coating formulations, in which a "two-component" system denotes a composition having a single base polymer and a cross-linking agent. Furthermore, traditional compositions also contain modifiers that promote adhesion or otherwise alter physical properties, and these additives also should not be confused with a second silicone component.

The advantages offered by the present invention stem, in part, from the use of a high-molecular-weight gum stock as a primary system component. Silicone gums having high dimethylsiloxane content can be used to create coatings that resist adhesion (that is, exhibit the property sometimes referred to as "abhesion") to compounds such as ink. We have also found that silicone-gum based polymeric systems are amenable to stable dispersion with solid particulates and can be applied with greater uniformity using a variety of coating lines as compared with lower-weight compositions. The former feature stands in marked contrast to polymers prepared from lower-weight silicones; as discussed above, such compositions are difficult to use the basis for dispersions.

**2073253**

On the other hand, silicone compositions prepared solely from gum stock tend to lack durability, particularly in the demanding environment of planographic printing. Our experience indicates that coatings prepared solely from the lower-weight polymers perform more durably, although these compositions tend to suffer from uniformity and dispersibility limitations. Furthermore, the viscosities of these low-molecular-weight polymers can be varied only within a limited range.

By combining these two components, we are able to achieve, in a single formulation, the advantages of compositions prepared from silicone gums and those prepared from lower-weight polymers, while minimizing the disadvantages associated with either type of composition individually. Specifically, we are able to disperse (and retain as dispersions) relatively large amounts of solids into our compositions, and control both system viscosity and durability by varying the proportions of the high-molecular-weight gum component (which exhibits high solution viscosity) and the low-molecular-weight component (which exhibits low solution viscosity and better durability characteristics).

In one embodiment of the invention, we vary the positions of each component's cross-linking constituents. For example, readily available gum compositions have functional (cross-linking) groups distributed along the chain, while it is possible to obtain lower-weight polymers with functional groups limited to the chain termini. Placement of identical functional groups at different positions within the molecular structures of the two components allows us to produce polymer systems consisting of two integrated networks that each combine differently with the cross-linking molecules, thereby contributing to the properties of the bulk material in different ways.



In another embodiment, we provide each component with a different functional group or groups, thereby retaining independent control over each component's interaction with cross-linking molecules. The cross-linking component can consist of a single molecular species that contains two different functional groups, each complementary to the functional group associated with one of the base polymers. The positions of the functional groups within each base polymer and within the cross-linking molecules can also be varied to achieve different physical properties.

Utilizing different functional groups for each component allows us to control the extent and rate of cure for each component independently of the other, since each component cross-links by a different chemical reaction. This "dual cure" capability allows us to combine, in one formulation, physical properties normally associated with a single type of cross-linking mechanism; it also affords greater flexibility in the choice of a coating deposition technique.

### C. Detailed Description of the Preferred Embodiments

The first base-polymer component of the compositions of the present invention is a high-molecular-weight polysiloxane compound with a molecular weight of at least 300,000, and preferably 500,000 or higher. The structure of this compound is generally linear. While it is possible to introduce a minor amount of branching, significant deviation from a linear structure decreases desirable properties such as good flow and elastomeric characteristics.

This first component preferably comprises a chain of dimethylsiloxane groups,  $[(CH_3)_2SiO]_n$ . However, we have also obtained advantageous results with copolymers of



2073253

-14-

dimethylsiloxane and higher methylalkylsiloxanes having up to 18 carbons in the alkyl group (larger alkyl groups tend to adversely affect ink-release and durability properties of the finished coating); phenylmethylsiloxanes; diphenylsiloxanes; and 3,3,3-trifluoropropylmethylsiloxane. Phenylmethyl and diphenylsiloxanes tend to confer heat tolerance, while the trifluoro compounds offer greatest resistance to most of the aliphatic and aromatic solvents that are commonly used to finely adjust the viscosity of the final silicone system, as well as to solvents found in printing inks. However, to preserve favorable ink-release properties, the proportion of dimethylsiloxane to other functional groups is preferably at least 70%. In the case of trifluoropropylmethylsiloxane, the proportion thereof to dimethylsiloxane can range up to 80%, while for phenylmethylsiloxane or diphenylmethylsiloxane groups the proportion to dimethylsiloxane preferably does not exceed 20%.

The first base-polymer component preferably contains functional groups randomly distributed along the polymer chain. Although in some cases it may be possible to utilize functional groups located at the chain termini of this component, we would expect to obtain less advantageous cross-linking structures using such compounds.

The functional group is introduced by incorporating substituted siloxane monomers into the polymerization reaction mixture, according to methods well-known in the art. The frequency of cross-linking (and, hence, the extent of curing) in the coating into which this component is introduced generally depends on the ratio of siloxane units containing functional groups to those which do not.

It is also possible to alter the physical properties of the cross-linked polymer while maintaining a constant mole

-15-

percentage of functional groups by utilizing disubstituted monomer units, thereby introducing two functional groups at a given chain position. Assuming the substituted monomers are randomly distributed along the polymer chain, this strategy results in greater spacing between the cross-linking sites but also creates locally higher cross-link density (because two functional groups are free to react) at each cross-linking position. Polymers produced using this disubstituted approach yield coatings that exhibit elasticities similar to those based on monosubstituted polymers having a similar weight percentage of functional groups (the greater spacing between reactive monomer units and locally higher cross-link densities tending to balance one another), and therefore retain good durability characteristics. Such compositions are particularly useful in the preparation of printing plates that employ flexible-film substrates, where elasticity of the coating is critical.

A wide range of complementary functional groups, and hence curing mechanisms, can be used with the present invention. For addition-cure coatings, our preferred functional group is vinyl; however, allyl (1-propenyl) and 1-butenyl groups are also readily employed as the two major components. Alternatively, it is possible to use higher alpha olefins up to 18 carbons as functional groups for addition-cure cross-linking. Such groups are advantageously employed in conjunction with a hydrogen-bearing cross-linking species, such as a polyhydrosiloxane (e.g., a polymethylhydrosiloxane polymer, copolymer or terpolymer), or a polyfunctional polysilane.

We also employ functional groups that are cross-linked by condensation-cure mechanisms, including silanols. For moisture-cure systems, the two major components contain silanol groups (i.e. hydroxyl functionalities), and the cross-linking component is hydrogen-bearing. Once again, suitable cross-



**2073253**

-16-

linking species include polymethylhydrosiloxane polymers, copolymers and terpolymers, and polyfunctional polysilanes. It is also possible to utilize functional groups curable by ultraviolet or electron-beam radiation (either directly or via activated photoinitiator species), e.g., acrylate, methacrylate or cycloaliphatic-epoxy species.

Preferably, the functional groups of the two major components are present on the polymer chains in amounts not exceeding 1.0 mole percent, with the range 0.1 to 0.5 mole percent being especially preferred; in the case of vinyl functionalities, the especially preferred range is 0.1 to 0.3 mole percent.

It is not necessary for all functional groups to be identical within a particular polymeric composition. By combining functional groups, we can exert control over the polymer networks that result from curing, and thereby improve selected properties of a formulation (e.g., expansion of the range of substrates to which the formulation can be applied). For example, if the functional groups of a single formulation include 75% vinyl and 25% alkoxy groups, one can first expose the polymer to addition-cure reaction conditions and then allow post-cure exposure of the coating to ambient air to trigger subsequent moisture cure (i.e., reaction of the alkoxy groups to produce additional cross-linking and bonding to the substrate).

In addition, by using such a dual-cure approach, we can obtain beneficial properties associated with two types of cross-linking molecules. For example, vinyl or other low-olefin groups tend to promote good adhesion properties, while acrylate and methacrylate cross-linkages tend to limit the degradative effects of solvent attack from printing inks. By combining these two groups within the first base-polymer



**2073253**

component, we are able to produce dry-plate coatings that repel ink while resisting attack from the very solvents that are probably responsible for the ink-repellent behavior. Furthermore, because the free-radical linkage mechanism of the acrylate and methacrylate groups do not interfere with or participate in the hydrosilylation reaction that cross-links the vinyl and hydrosiloxane groups, these reactions are compatible with one another. It is also possible to utilize unmodified hydrosiloxane cross-linking molecules with this dual-cure reaction, since the acrylate and methacrylate groups react with one another directly (in the presence of suitable initiators).

The second base-polymer component of our formulations is a relatively light polysiloxane compound with a molecular weight up to 70,000. Preferably, the structure of this compound is also substantially linear, although once again it is possible to introduce a minor amount of branching. The functional-group characteristics described above with regard to the first component apply as well to this second component. However, it is preferable to have the functional groups in this second component situated at the ends of the polymer chains. This positioning has been found to promote durability, while random distribution along the chain produces brittle compositions in combination with the first base-polymer discussed above.

The relative proportions of the primary and secondary components can be varied over a wide range, allowing significant variation in the viscosities, dispersibilities, dispersion stabilities and solids contents of the final coatings obtainable using the present invention. Our preferred working range allows variation in the relative proportions, in weight percent, of each component from 10% to 90% (i.e. 10% first component and 90% second component to 90% first component

-18-

and 10% second component).

The cross-linking species of the present invention is preferably a monomeric or oligomeric polysiloxane that contains functional groups complementary to those of the base-polymer components. Preferably, the molecular weight of the cross-linking agent is between 2,000 and 5,000, although oligomers with molecular weights of 500 or even less may be usable under some circumstances; if the molecular weight of the cross-linking species is too low for the curing procedure employed, excessive amounts will evaporate from the reaction mixture during curing.

The fastest (and therefore practical) cure times are obtained with relatively large numbers of functional groups distributed along the chains of the cross-linking component. However, while cross-linking molecules containing only terminal functional groups require significant reaction times, the compositions produced therewith tend to exhibit excellent elastomeric properties. Accordingly, our preferred route use a limited number of functional groups spaced as widely along the cross-linking chains as possible, the precise numbers and configuration being dictated by the user's reaction-time constraints.

If pigments or other solids are to be introduced into the final formulation, these can be dispersed within one of the components (preferably the high-molecular-weight first component) prior to combination of the two components, or within the final formulation after combination.

We will now describe preparation of several representative formulations.



-19-

EXAMPLES 1-4

In each of these four examples, a pigment was initially dispersed into the high-molecular-weight gum component, which was then combined with the second component. For the gum component, we utilized a linear, dimethylvinyl-terminated polydimethylsiloxane supplied by Huls America, Bristol, PA under the designation PS-255\*. For each formulation, the gum component was combined with one of the following pigments:

<u>Pigment</u>	<u>Trade Name</u>	<u>Supplier</u>
ZnO	Kadox* 911	Zinc Corp. of America Monaca, PA
Fe <sub>3</sub> O <sub>4</sub>	BK-5000*	Pfizer Pigments, Inc. New York, NY
SnO <sub>2</sub> -based	CPM 375*	Magnesium Elektron, Inc. Flemington, NJ
SnO <sub>2</sub> -based	ECP-S* Micronized	E.I. duPont de Nemours Wilmington, DE

Each pigment was used to prepare a different formulation. First, pigment/gum dispersions were prepared by combining 50% by weight of each pigment and 50% by weight of the gum in a standard sigma arm mixer.

Next, the second component was prepared by combining 67.2% by weight of the mostly aliphatic (10% aromatic content) solvent marketed by Exxon Company, USA, Houston, TX under the trade name VM&P Naphtha with 16.9% of the vinyl-dimethyl-terminated polydimethylsiloxane compound marketed by Huls

\*Trade-mark



-20-

America under the designation PS-445\*, which contains 0.1-0.3% methylvinylsiloxane comonomer. The mixture was heated to 50-60 degrees Centigrade with mild agitation to dissolve the PS-445.

In separate procedures, 15.9% by weight of each pigment/gum dispersion was slowly added to the dissolved second component over a period of 20 minutes with agitation. Agitation was then continued for four additional hours to complete dissolution of the pigment/gum dispersions in the solvent.

After this agitation period, 0.1% by weight of methyl pentynol was added to each blend and mixed for 10 minutes; after which 0.1% by weight of PC-072\* (a platinum-divinyldtetramethyldisiloxane catalyst marketed by Huls) was added and the blends mixed for an additional 10 minutes. The methyl pentynol acts as a volatile inhibitor for the catalyst. At this point, the blends were filtered and labelled as stock coatings ready for cross-linking and dilution.

To prepare batches suitable for wire-wound-rod or reverse-roll coating applications, the stock coatings prepared above were each combined with VM&P Naphtha in proportions of 100 parts stock coating to 150 parts VM&P Naphtha; during this step, the solvent was added slowly with good agitation to minimize the possibility of the solvent shocking (and thereby disrupting) the dispersion. To this mixture was added 0.7 parts PS-120\* (a polymethylhydrosiloxane cross-linking agent marketed by Huls) under agitation, which was continued for 10 minutes after addition to assure a uniform blend. The finished coatings were found to have a pot life of at least 24 hours, and were subsequently cured at 300 degrees Fahrenheit for one minute.

\*Trade-mark

-20a

EXAMPLES 5-7

In each of these next examples, commercially prepared pigment/gum dispersions were utilized in conjunction with a second, lower-molecular-weight second component. The pigment/gum mixtures, all based on carbon-black pigment, were

\*Trade-mark

-21-

obtained from Wacker Silicones Corp., Adrian, MI. In separate procedures, we prepared coatings using PS-445 and dispersions marketed under the designations C-968, C-1022 and C-1190 following the procedures outlined above (but omitting the dispersing step). The following formulations were utilized to prepare stock coatings:

<u>Order of Addition</u>	<u>Component</u>	<u>Weight Percent</u>
1	VM&P Naphtha	74.8
2	PS-445	18.0
3	Pigment/Gum Dispersion	7.0
4	Methyl Pentynol	0.1
5	PC-072	0.1

Coating batches were then prepared as described above using the following proportions:

<u>Component</u>	<u>Parts</u>
Stock Coating	100
VM&P Naphtha	100
PS-120 (Part B)	0.6

The three coatings thus prepared were found to be similar in cure response and stability to Examples 1-4.

#### EXAMPLE 8

The formulations described above undergo cross-linkage by addition-cure hydrosilylation reactions. It is possible to replace the olefin-functional groups with silanol groups to facilitate a condensation-cure mechanism, even utilizing the



**2073253**

-22-

same PS-120 cross-linking agent. One approach to condensation cure is use of alkoxy functional groups to facilitate cure by exposure to moisture.

Dispersion of a pigment into a silanol-functional high-molecular-weight polymer is accomplished in the same manner as described in Examples 1-4. If PS-445 is retained as the low-molecular weight component, dual-cure is possible; replacing the olefin-functional PS-445 with a silanol-functional (or alkoxy-functional) silicone results in a single-cure reaction analogous to those described above.

Cross-linking to the silanol-functional groups is accelerated by a catalyst such as a dialkyltindicarboxylate (e.g., dibutyltindiacetate), a metal carboxylate (e.g., zinc dioctoate), a titanate, or a thermally activated latent catalyst (e.g., as described in published European Patent Application 338,947). None of these catalysts would be expected to interfere with the addition-cure components described above, thereby facilitating a dual-cure system. With this approach, the olefin-functional secondary component is subjected to the cross-linking conditions described in Examples 1-4 before silanol cross-linking.

#### EXAMPLE 9

We compared the solids content of an unpigmented coating prepared using our two-component approach to an unpigmented coating having similar viscosity but based entirely on the low-molecular-weight PS-445. Both coatings were prepared using the techniques outlined in Examples 1-4, but omitting the pigment-dispersion step. The proportions of reactants utilized in each of the coatings were as follows:

-23-

<u>Component</u>	<u>Weight Percent</u>	
	<u>Coating 1</u>	<u>Coating 2</u>
VM&P Naphtha	90.63	83.9
PS-445	4.5	15.5
PS-255	4.5	--
Methyl Pentynol	0.05	0.05
PC-072	0.05	0.05
PS-120	0.27	0.5

Coating 1 and Coating 2 exhibit equivalent viscosities and can be applied using the same coating technique to yield similarly uniform coatings. However, the solids content of Coating 2 -- which represents a typical single-component approach -- is approximately twice that of Coating 1. Furthermore, because both the viscosity and solids content of Coating 2 depend entirely on the proportion of a single silicone component, coating viscosity requirements impose a significant limitation on the degree to which solids content can be altered.

By contrast, the formulation of Coating 1 can be altered by changing the relative proportions of PS-445 and PS-255, retaining a consistent viscosity while varying solids content. This is shown in the following two variations of Coating 1, one (Coating LS) formulated for low-solids content, and the other (Coating HS) formulated for high-solids content.

-24-

<u>Component</u>	<u>Weight Percent</u>	
	<u>Coating LS</u>	<u>Coating HS</u>
VM&P Naphtha*	92.7	84.45
PS-445	1.0	13.0
PS-255	6.0	2.0
Methyl Pentynol	0.05	0.05
PC-072	0.05	0.05
PS-120	0.2	0.45

After solvent evaporation, Coating LS will deposit less than half the weight of silicone that would be deposited by Coating HS.

#### EXAMPLE 10

We modified Coating 1 of the previous example to obtain a diphenylsiloxane composition by replacing the PS-445 second component with an equivalent weight percentage of PS-767.5, also marketed by Huls. PS-767.5 is a vinyl-terminated 4-6% diphenylsiloxane, 94-96% dimethylsiloxane copolymer.

The physical characteristics of this coating were similar to those of Examples 1-4, but would be expected to exhibit greater heat tolerance.

#### EXAMPLE 11

We modified Coating 1 of the previous example to obtain a trifluoro composition by replacing the PS-445 second component with an equivalent weight percentage of PLY-7801\*, marketed by McGhan Nusil Corp. of Carpinteria, CA, and

\*Trade-mark



**2073253**

-25-

replacing the VM&P Naphtha with an equivalent weight percentage of 1,1,1-trichloroethane.

EXAMPLE 12

We modified Coating LS of the previous example to obtain a dual-cure composition by replacing the PS-445 second component with an equivalent weight percentage of PS-344.5, and replacing the PS-120 cross-linking agent with an equivalent weight percentage of PS-128; all components were supplied by Huls. PS-344.5 is a silanol-terminated polydimethylsiloxane compound, and PS-128 is a methyldimethoxy-terminated polymethylhydrosiloxane compound. Moisture activates the methoxy-silanol condensation reaction, which benefits from the acidic by-products of the chloroplatinic acid catalyst (PC-072) that accelerates the addition-cure reaction between the vinyl groups of the gum component and the hydrosiloxane groups of the cross-linking molecules.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. For example, for production-scale coating preparation, it may be advantageous to add the second component directly to the gum/pigment dispersion to produce an easily handled paste; alternatively, it might prove desirable to add the solvent directly to the gum/pigment dispersion, or to add both the solvent and second component simultaneously.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A polymeric silicone composition comprising:
  - a. a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain;
  - b. a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one functional group; and
  - c. a cross-linking component having functional groups complementary to those of the first and second polysiloxane components.
2. The composition of claim 1 wherein the mole ratio of siloxane units containing a functional group to those which do not range from approximately 0.1 to 1.0.
3. The composition of claim 1 wherein the relative weight proportion of the first polysiloxane component with respect to the second polysiloxane component ranges from 10% to 90%.



4. The composition of claim 1 wherein the siloxane units include dimethylsiloxane units.
5. The composition of claim 4 wherein at least 70% of the substituted siloxane units are dimethylsiloxane units.
6. The composition of claim 1 wherein the first molecular component has a molecular weight of at least 500,000.
7. The composition of claim 4 wherein the siloxane units also

include higher alkylmethoxysiloxane units, the alkyl group having up to 18 carbons.

8. The composition of claim 4 wherein the siloxane units also include phenylmethoxysiloxane units.

9. The composition of claim 4 wherein the siloxane units also include diphenylsiloxane units.

10. The composition of claim 4 wherein the siloxane units also include 3,3,3-trifluoropropylmethoxysiloxane units.

11. The composition of claim 10 wherein up to 80% of the substituted siloxane units are 3,3,3-trifluoropropylmethoxysiloxane units.

12. The composition of claim 8 wherein the proportion of phenylmethoxysiloxane units to dimethoxysiloxane units does not exceed 20%.

13. The composition of claim 9 wherein the proportion of diphenylsiloxane units to dimethoxysiloxane units does not exceed 20%.

14. The composition of claim 10 wherein the proportion of 3,3,3-trifluoropropylmethoxysiloxane units to dimethoxysiloxane units does not exceed 80%.

15. The composition of claim 1 wherein at least one functional group of the first polysiloxane component is the same as at least one functional group of the second polysiloxane component.

16. The composition of claim 1 wherein no functional group of the first polysiloxane component is the same as any functional

group of the second polysiloxane component.

17. The composition of claim 1 wherein more than one type of functional group is present in either of the first and second components or in both components.

18. The composition of claim 17 containing two types of functional group, wherein one type of functional group cross-links by an addition-cure mechanism and the other type of functional group cross-links by a moisture-cure mechanism.

19. The composition of claim 17 containing two types of functional group, wherein one type of functional group is a low olefin and the other type of functional group is an acrylate or a methacrylate.

20. The composition of claim 19 wherein the low olefin is distributed along the chains of the first component and the acrylate or methacrylate group is linked to the termini of the chains of the second component.

21. The composition of claim 1 wherein each functional group of the first and second components is capable of reacting with the functional groups of the cross-linking component via addition cure.

22. The composition of claim 1 wherein each functional group of the first and second components is capable of reacting with the functional groups of the cross-linking component via condensation cure.

23. The composition of claim 1 wherein each functional group of the first and second components is capable of reacting with the functional groups of the cross-linking component via moisture cure.



24. The composition of claim 1 wherein each functional group of the first and second components is capable of reacting with the functional groups of the cross-linking component via initiation by ultraviolet radiation.
25. The composition of claim 1 wherein each functional group of the first and second components is capable of reacting with the functional groups of the cross-linking component via initiation by electron-beam radiation.
26. The composition of claim 1 wherein each functional group of the first component is selected from the group consisting of vinyl, low olefins, silanol, cycloaliphatic epoxy, acrylates and methacrylates.
27. The composition of claim 1 wherein each functional group of the second component is selected from the group consisting of vinyl, low olefins, silanol, cycloaliphatic epoxy, acrylates and methacrylates.
28. The composition of claim 21 wherein each functional group of the first and second components is a low olefin and the cross-linking component is a polymethylhydrosiloxane polymer, copolymer or terpolymer.
29. The composition of claim 28 wherein the low olefin is selected from the group consisting of vinyl, allyl and butenyl.
30. The composition of claim 22 wherein each functional group of the first and second components is hydroxyl and the cross-linking component is a polymethylhydrosiloxane polymer or copolymer.
31. The composition of claim 22 wherein each functional group

of the first and second components is hydroxyl and the cross-linking component is a polyfunctional silane.

32. The composition of claim 22 wherein each functional group of the first and second components is hydroxyl and the cross-linking component is a polyfunctional polysiloxane.

33. The composition of claim 23 wherein each functional group of the first and second components is hydroxyl and the cross-linking component is a polyfunctional silane.

34. The composition of claim 23 wherein each functional group of the first and second components is hydroxyl and the cross-linking component is a polyfunctional polysiloxane.

35. The composition of claim 24 wherein each functional group of the first, second and cross-linking components is an acrylate species.

36. The composition of claim 24 wherein each functional group of the first, second and cross-linking components is a methacrylate species.

37. The composition of claim 24 wherein each functional group of the first, second and cross-linking components is a cycloaliphatic epoxy species.

38. The composition of claim 25 wherein each functional group of the first, second and cross-linking components is an acrylate species.

39. The composition of claim 25 wherein each functional group of the first, second and cross-linking components is a methacrylate species.

40. The composition of claim 1 further comprising a pigment dispersed therein.

41. A method of preparing a coating composition, the method comprising the steps of:

- a. combining, to form a mixture, a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain; a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one functional group; and a cross-linking component having functional groups complementary to those of the first and second polysiloxane components;
- b. combining the mixture with a solvent; and
- c. curing the mixture.

42. The method of claim 41 further comprising the step of dispersing a pigment into the mixture.

43. The method of claim 41 wherein the mixture is cured using a catalyst.

44. The method of claim 41 wherein the mixture is cured using ultraviolet radiation.



45. The method of claim 41 wherein the mixture is cured using electron-beam radiation.

46. A planographic printing plate capable of being imaged, comprising a substrate having applied to at least one surface thereof a polymeric silicone composition which itself comprises:

a. a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain;

b. a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one functional group; and

c. a cross-linking component having functional groups complementary to those of the first and second polysiloxane components.

47. The plate of claim 46 wherein the substrate is an oleophilic material and further comprising a metal layer disposed between the substrate and the polymeric silicone composition.

48. The plate of claim 46 wherein the silicone composition further comprises a pigment dispersed therein.

C

49. A method of preparing a planographic plate comprising coating at least one surface of a substrate with a polymeric silicone composition which itself comprises:

a. a first polysiloxane component having a molecular weight in excess of 300,000 and comprising substantially linear chains of substituted siloxane units, a plurality of which contain at least one functional group and are randomly interspersed in the chain;

b. a second polysiloxane component having a molecular weight no greater than 70,000 and comprising substantially linear chains of substituted siloxane units capped by terminal siloxane units containing at least one functional group; and

c. a cross-linking component having functional groups complementary to those of the first and second polysiloxane components.

50. The method of claim 49 wherein the substrate is an oleophilic material and further comprising the step of introducing a metal layer on one surface of the substrate prior to coating with the polymeric silicone composition, and subsequently coating the metal layer with the polymeric silicone composition.

SMART & BIGGAR  
OTTAWA, CANADA

PATENT AGENTS