Silicone Polymers in Fabric Softeners

IIPRD

PATENT LANDSCAPE REPORT – SILICONE POLYMERS IN FABRIC SOFTENERS
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1. Introduction

Fabric Softener
Fabric softeners are widely used by home consumers and commercial laundries to provide softness, surface smoothness, good draping qualities, fluffiness and antistatic properties while avoiding surface greasiness or excessive build-up on the fabric. Although fabric softener technology is well known, the exact softening mechanism is not known. One commonly accepted mechanism relates softness to the lubricity of the adsorbed softener on the cloth and the consequent reduction of friction between the fabric fibers. Furthermore, softeners have gained great importance in textile finishing. This softening treatment aims to improve the handling properties of textiles and to make the process easier.

Silicones in Fabric Softeners
The use of silicones for softening fabrics has been well known for quite some time. In addition, the use of organo modified silicones for textile treatments has also been well documented over the years. It is also known to treat fibrous materials such as textiles with polysiloxanes to impart desirable properties such as water repellency, lubricity and crease resistance. Deposition of silicone polymers on the fibers results in a very good spreading action and excellent lubrication properties. This is mainly due to high flexibility of Si-O-Si backbone of silicone polymers. Furthermore, this deposition behaviour can be controlled by means of functional group and molecular weight modifications.

Silicones are one of the most commonly known polymers in textile industries. Silicones enhance value of the fabric by transforming fabric handle to match customer perception. Silicones are organo metallic polymers derived from the abundant raw material on earth, sand etc. Silicone is a polymer which is primarily based on a frame work of alternating silicon and oxygen (Siloxane Bonds) with organic substituents attached to the silicon. Methyl groups are the most important organic substituents used in the commercial silicones which majorly include Polydimethylsiloxanes.

Silicones exhibits some unique properties including thermal oxidative stability, low temperature flow ability, low viscosity change against temperature, high compressibility, low surface tension, hydrophobicity, good electric properties and low fire hazard because of their Inorganic– Organic structure and the flexibility of the silicone bonds. One of the key features of silicone materials is effectiveness at very low concentrations. Very small amounts of
silicones are required to achieve the desired properties, which can improve the cost of textile operations and ensure a minimum environmental impact.

Silicones
More precisely called polymerized siloxanes or polysiloxanes, silicones are mixed inorganic-organic polymers with the chemical formula \([R2SiO]n\), where \(R\) is an organic group such as methyl, ethyl, or phenyl. These materials consist of an inorganic silicon-oxygen backbone (\(\cdots\text{Si-O-Si-O-Si-O}\cdots\)) with organic side groups attached to the silicon atoms, which are four-coordinate.

In some cases, organic side groups can be used to link two or more of these -Si-O-backbones together. By varying the -Si-O-chain lengths, side groups, and crosslinking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic.

Polydimethylsiloxanes
The most common siloxane is linear polydimethylsiloxane (PDMS), silicone oil. Polydimethylsiloxanes are available in viscosities ranging from 0.65 cSt to 1,000,000 cSt for methyl terminated polymers and from 70 cSt to 330,000 for polymers terminated with hydroxyl groups. The Addition of Polydimethylsiloxane to fabric softener formulations dramatically improves the water absorbency of softened cotton fabric. The Diverse property of the silicone can be changed by changing the R group in the structure.

Fig 1: Structure of polydimethylsiloxane

Where \(X\) and \(Y\) = number of monomeric units

Amino-functional silicones
Mostly amino modified silicones are used in textile industry as amino groups provide better affinity to textile fibers. For further reactivity the end group of the amino silicone polymer
needs to be hydroxyl, methoxy, ethoxy, but if the end group is methyl group then the polymer is called as non reactive or terminated one. The high bonding affinity of the amine polymers makes them more substantive to fabrics than the other silicone polymers. In general the amino functional silicones reach their best performance after 2-3 washes. Yellowing may be resulting when amino silicones are used on white garments due to the oxidation of amino radicals in the presence of air, heat and light energy which results in the formation of azoxy compounds.

**Fig 2: Structure of an amino-functional silicone**

\[
\begin{align*}
 & \text{Si-O-CH}_3 \\
 & \text{Si-O-CH}_3 \\
 & \text{Si-O-CH}_2 \text{NH}_2
\end{align*}
\]

Where X and Y = number of monmeric units

**Amido-functional silicones**

Amido functional silicones have limited range of viscosities and nitrogen content. The benefits of amido silicones are highly effective softening, ease of ironing, water absorbency and low yellowing. They are more substantive to fabrics than polydimethylsiloxanes.

**Fig 3: Structure of an amido-functional silicone**

\[
\begin{align*}
 & \text{Si-O-CH}_3 \\
 & \text{Si-O-CH}_2 \text{NH} \\
 & \text{Si-O-CH}_2 \text{NH}_2 \\
 & \text{Si-O-CH}_2 \text{NH》}
\end{align*}
\]
Other modifications to silicone

The diverse properties of the silicone can be changed by changing the R group in the general structure of silicone. Given below are the properties derived by incorporating different modifications.

<table>
<thead>
<tr>
<th>Silicone</th>
<th>Properties derived</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino Group</td>
<td>Highly exhaustible and durable softness</td>
</tr>
<tr>
<td>Hydrophilic Group</td>
<td>Water adsorptive</td>
</tr>
<tr>
<td>Methyl Group</td>
<td>Water repellence and antistatic finish</td>
</tr>
<tr>
<td>Hydrogen Group</td>
<td>Water repellence and soil resistance</td>
</tr>
<tr>
<td>Other Organo modifications</td>
<td>Drapery and wrinkle recovery property</td>
</tr>
</tbody>
</table>

Silicone Emulsions

Polydimethylsilicones, amino and amido functional silicones are stabilized by adding an emulsifier or emulsifying agents. All emulsifying agents concentrate at and are located adsorbed onto the oil water interface to provide a protective barrier around the dispersed droplets. In addition to this protective barrier, emulsifiers stabilize the emulsion by reducing the interfacial tension of the system. Some agents enhance the stability by imparting a charge on the droplet surface thus reducing the physical contact between the droplets and decreasing the potential for coalescence. The Emulsion characteristics in particular their particle size and the surfactant system used play a critical role both in terms of deposition on the fabric and the stability in the final product. Micro emulsions typically have a particle size below 100 nm which can penetrate into the yarns and can deposit onto fabric fibers. In Contrast macro emulsions deposit on the external surface of the fabric. Cationic emulsions have a very good compatibility with fabric softeners and provide very high level of silicone deposition. Non Ionic Emulsions have good stability. Anionic emulsions generally show good compatibility with standard detergent but have an uncertain deposition.
2. Scope and Coverage

The analysis covered worldwide patents and patent applications filed from 2003 to the present, pertaining to the use of silicone polymers in the production of fabric conditioners.

Geographies covered:

- United States of America (US)
- European Union (EP)
- Patent cooperation treaty (PCT)
- Canada (CA)
- Japan (JP)
- India (IN)
- Other countries
3. Research Methodology

The following search methodology was adopted for the patent landscape analysis:

- Identifying relevant keywords and patent classification codes pertaining to silicone polymers in fabric softeners (Refer Appendix 1)
- Conducting State-Of-the-Art search pertaining to said subject matter
- Creating various technology clusters and sub clusters in view of the said subject (Refer Section 4)
- Analyzing and clustering the relevant patent documents into various technology buckets
- Statistical analysis (Refer Section 6)
- Assignee analysis (Refer Section 7)
- Report generation
4. Technology Clusters

The relevant patent families identified from the State-Of-the-Art search were clustered into the following technology clusters.
5. Research Findings

The indicative search strategy (Refer Appendix 3) framed for conducting the landscape analysis yielded a total of **1,430 patent documents** from the ORBIT database. The subsequent in-depth analysis of the above patent dataset resulted in **375 relevant patent families**. The relevant patent families disclose different types of fabric care compositions and formulations which contain various types of silicone polymers viz. polydimethylsiloxane (PDMS), amine-functional silicones, amide-functional silicones, polyether modified silicones, etc... All these 375 patent families were further clustered into various technology buckets (Refer Section 4).

6. Statistical analysis

6a. Overall Patent Filing Trends Across Years

The patent filing trend study has considered all 375 patent families for the analysis. It is observed from the above analysis that patent filing activities were highest in the year of 2013 and 2011 with 53 and 50 patents respectively. It is also observed that the patent filing activities were consistent from 2003 to 2010 with more than 20 patents per year, indicating consistent research work in the subject technical domain.
6b. Patent Filings across Major Geographies

Below is an overview of the geographical distributions of the patent filings to provide insight into how many patents have been filed in the field of silicone polymers in fabric softeners during the last 10 years. The analysis has considered only the total number of patents filed in major geographies viz. United States, Europe, Canada, Japan, Germany, Korea, India, Brazil, Spain and the Patent cooperation treaty (WO).

It is observed from the analysis that two countries viz. United States of America (US) and Japan to top the list with 121 and 120 patent publications respectively. Europe identified to be the next major country with 108 patent publications. With 116 patent publications, PCT (WO) found to be the most preferred route to file patent applications. Other countries viz. CA, DE, KR, IN, BR and ES follow the trend with 69, 38, 35 and 32 patent publications respectively. Brazil and India found to be the least preferred geographies with 20 and 15 patent publications respectively.
6c. Technology Mapping

The analysis has revealed that amino-functional silicones were the most targeted area in the fabric conditioner segment with 139 patent families. Next to amino-functional silicones, polydimethylsiloxane is the more preferred chemical in the organo-functional siloxane family with 109 patent families.

Surprisingly other types of organo-functional siloxanes viz. amide-functional silicones, polydimethyldiphenylvinylsiloxane, epoxy modified silicones, polyether modified, hydroxy silicone, etc. were the least preferred silicones in the fabric softener industry during the last decade.

It is observed from the technology mapping analysis that, research work has concentrated on the aqueous delivery of these silicone systems via macroemulsions in the last decade.
6d. IPC Analysis

The graph represents the various international class codes distributions versus silicon polymers in fabric softeners. It is an overview to provide insight into the number of IPC’S used in the field of Silicone Polymers pertaining to fabric softeners during the last decade.
7. Assignee Analysis

The assignee analysis on the 375 patent families revealed that 314 patent families held by companies. Out of 376 patent families, 37 patent families held by Universities or research institutes, while individual inventors hold 24 patent families.

Patent filings by key companies:

An overview of the numbers of patent publications related to “Silicone polymers in fabric softeners” from primary and secondary assignees during last ten years is provided below. The companies which filed 20 or more patents during the investigative period have been considered as primary assignees, while companies filed 5 to 19 patents during the investigative period have been considered as secondary assignees.

Primary Assignees:

Primary assignees give an overview of the top players in the particular technological domain

<table>
<thead>
<tr>
<th>S.No</th>
<th>Company Assignees</th>
<th>Patent Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PROCTER &amp; GAMBLE</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>LION Corporation</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>KAO</td>
<td>20</td>
</tr>
</tbody>
</table>
Secondary Assignees:

Secondary assignees are those players who have a limited interest in this particular technological domain.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Company Assignees</th>
<th>Patent Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SANYO CHEMICAL INDUSTRIES</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>UNILEVER</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>DOW CORNING</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>EVONIK DEGUSSA GMBH</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>ZHANGJIAGANG DUPLUS CHEMICAL</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>ECOLAB</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>HENKEL</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>HUANGSHAN QIANGLI CHEMICAL</td>
<td>5</td>
</tr>
</tbody>
</table>
8. Conclusion

- Amino-functional silicone and polydimethylsiloxane based fabric softeners are the highly patented technologies during the last ten years.

- Over the last 10 years, there have been many patents published in the area of silicone macroemulsions. The research reveals that silicone macroemulsions effectively reduces the fiber to fiber and/or yarn to yarn friction as compared to microemulsions when used with a fabric softener.

- PROCTER & GAMBLE, LION CORPORATION and KAO are the key players in the silicon based fabric softener segment.

- Among various countries, United States of America, Japan and Europe have the highest number of patent filings within the field of silicone based fabric softeners.
9. Appendix

Appendix 1: List of Relevant Patents

This section provides the list of the relevant patent documents filed from 2003 to the present, pertaining to the use of various types of silicone polymers in the production of fabric conditioners.

Note: This being an exemplary report, we have listed only one patent as sample. Complete list of relevant patent documents can be provided on request.

Reference Document: 1

<table>
<thead>
<tr>
<th>Patent number</th>
<th>EP2196527A1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title</td>
<td>Fabric softening compositions comprising silicone comprising compounds</td>
</tr>
<tr>
<td>Assignee</td>
<td>Proctor &amp; Gamble</td>
</tr>
<tr>
<td>Abstract</td>
<td>The present invention relates to a fabric softening composition which maintains physical stability upon freeze-thaw. The composition comprises a fabric softening active, 0.5 to 10% by weight of a silicone comprising compound, 0.005 to 4% by weight of a non-ionic alkoxyalted surfactant, and 0.005 to 15% by weight of a polyol.</td>
</tr>
<tr>
<td>Image</td>
<td><img src="image.png" alt="Image" /></td>
</tr>
</tbody>
</table>

FIG. 1
Reference Document: 2

<table>
<thead>
<tr>
<th>Patent number</th>
<th>JP2008121151</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title</td>
<td>Textile Product Treating Agent</td>
</tr>
<tr>
<td>Assignee</td>
<td>KAO CORPORATION</td>
</tr>
<tr>
<td>Family members</td>
<td>JP5000271</td>
</tr>
</tbody>
</table>

**Abstract**

To provide a textile product treating agent having high softening effects and sufficiently exhibiting a feeling unique to a silicone. **SOLUTION:** The textile product treating agent comprises a silicone compound and a polymer containing a monomer constituent unit derived from a compound of general formula (1) [wherein \( R^{(1)} \) and \( R^{(5)} \) are each hydrogen atom or methyl group; \( Y \) is selected from among \(-\text{COOR}^{(4)}\), \(-\text{CON}(R^{(5)})R^{(6)}\), \(-\text{OCOR}^{(7)}\) and \(-\text{CH}_{(2)}\); \( R^{(2)} \) is \( \text{CH}_{(2)}\)=C\((R^{(1)})\)-CH\(_{(2)}\)- when \( Y \) is \(-\text{CH}_{(2)}\); \( R^{(2)} \) and \( R^{(3)} \) are each an alkyl group or the like in the other case; and \( R^{(4)} \), \( R^{(6)} \) and \( R^{(7)} \) are each an alkylene group].

![Chemical structure](image)
<table>
<thead>
<tr>
<th>Patent number</th>
<th>JP2007063741</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Title</strong></td>
<td>Liquid Softening Agent Composition</td>
</tr>
<tr>
<td><strong>Assignee</strong></td>
<td>LION</td>
</tr>
<tr>
<td><strong>Family members</strong></td>
<td>WO2008018186, KR20090037912, JP5328084</td>
</tr>
<tr>
<td><strong>Abstract</strong></td>
<td>Disclosed is a liquid softener composition which can inhibit unpleasant odor formed from laundry and whose perfume is less likely to remain on cloths. The liquid softener composition comprises: (A) a silicone polymeric compound; (B) a cationic water-soluble polymeric compound; and (C) a perfume composition comprising a perfume component having a boiling point of 250°C or lower.</td>
</tr>
</tbody>
</table>

![Chemical Structure](image-url)
Appendix 2: Search Strategy

Keyword based analysis
One or more of the keywords listed below have been used in different combinations while conducting the search:

Keywords
- Silicone / Organo Siloxane/ Poly Alkyl Siloxane/ Amino Siloxane/ Amido Siloxane
- Textile / Cloth / Fabric / Fibre / Fiber / Yarn / Cotton / Wool / Nylon / Polyester / Silk
- Softener / Conditioner / Softer / Lubricant / Friction reducer / Static cling / Lubricity

IPC Codes
One or more of the IPC listed below have been used in different combinations while conducting the search:

<table>
<thead>
<tr>
<th>IPC</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11D</td>
<td>DETERGENT COMPOSITIONS; USE OF SINGLE SUBSTANCES AS DETERGENTS; SOAP OR SOAP-MAKING; RESIN SOAPS; RECOVERY OF GLYСEROL</td>
</tr>
<tr>
<td>D06</td>
<td>TREATMENT OF TEXTILES OR THE LIKE; LAUNDERING; FLEXIBLE MATERIALS NOT OTHERWISE PROVIDED FOR</td>
</tr>
<tr>
<td>D06M</td>
<td>TREATMENT, NOT PROVIDED FOR ELSEWHERE IN CLASS D06, OF FIBRES, THREADS, YARNS, FABRICS, FEATHERS OR FIBROUS GOODS MADE FROM SUCH MATERIALS (treatment of textiles by mechanical means D06B-D06J)</td>
</tr>
<tr>
<td>D06L</td>
<td>BLEACHING, e.g. OPTICAL BLEACHING, DRY-CLEANING OR WASHING FIBRES, THREADS, YARNS, FABRICS, FEATHERS OR MADE-UP FIBROUS GOODS; BLEACHING LEATHER OR FURS (chemical treatment of fibrous materials to obtain fibres for spinning D01; for mechanical matters D06B, D06C, D06F; bleaching paper pulp or cotton linters D21)</td>
</tr>
</tbody>
</table>
### Appendix 3: Search strings

Database: ORBIT

Time scope: 2003 – Aug 2014

<table>
<thead>
<tr>
<th>INDICATIVE SEARCH STRING</th>
<th>HITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(((SILICONE OR SILOXANE) AND ((SOFT+ OR CONDITION+ OR LUBRIC+ OR FRICTION OR (STATIC 1W CLING)) 20D (FABRIC+ OR TEXTILE+ OR CLOTH+ OR FIBRE+ OR YARN+ OR COTTON+ OR WOOL+ OR NYLON+ OR POLYESTER+ OR SILK+ OR FIBER+))) )/BI/CLMS AND ((D06+ OR C11D+)) )/IPC AND PRD &gt;= 2003</td>
<td>1,430</td>
</tr>
</tbody>
</table>
10. Disclaimer

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