

Textile industry softeners and latest developments

K H Prabhu

Senior Technologist, Dyeing & Finishing, Texcoms Textile Solutions, Singapore
prabhu@texcoms.com

A large number of consumers in the fast fashion world uses different sets of apparels and textile products for different end uses, namely nightwear, office wear, children's wear, winter or summer wear,

is a unique selling point (USP) parameter that leads to a final purchase decision¹. On the other hand, during initial pretreatment preparation, textiles can become harsh since natural oils and waxes are removed. Finishing with softeners can



gym wear etc. The most important and basic requirement of these garments are functional properties such as quick dry, crease resistance, antibacterial finish, aroma control etc. However, the most precisely important property is the softness of the material which often seems to be final decision of the consumer. Today, wearers give more importance to garment feel and comfort along with the aesthetic appeal. Thus, the apparel manufacturers are very careful in terms of providing a good softening finish with good durability without losing other performance properties. Overall, a 'softer feel'

overcome this deficiency and even improve on the original suppleness. For all these reasons, today softening of textiles is an important and essential finishing process.

Development of greener and ecofriendly softeners will reduce the environmental issues

Softeners

By definition, softeners are a chemical or blend of chemicals which, when applied to textile

materials, brings about a change of handle that is more pleasing to the touch, although the notion of 'pleasing to the touch' varies from person to person².

Softeners are predominantly used for textiles³:

- to apply the desired softness such as smooth, supple, super soft, elastic, dry, slushy etc
- to improve functional properties such as antistatic, hydrophilicity, elasticity, sewability, rub fastness etc
- to give natural touch and enhance the comfort properties (moisture regulation, smoothness etc) of synthetic fibre wearers.

Major requirement of textile softeners³

- Simple handling and stable to high temperatures; not steam volatile
- No influence on fastnesses; no colour changes
- Low foaming; shear stable; no roller deposits
- Exhaust processes - uniform and total exhaustion of application liquor
- Non-toxic to humans or to the environment and compatible with other auxiliaries
- Non-yellowing
- Dermatologically harmless
- Good biodegradability.

Chemistry

Most of the softeners consist of molecules with both, a hydrophobic and a hydrophilic characteristic. Hence, they can be alternatively termed as surfactants (surface active agents). Typically, a softener contains a long alkyl group, sometimes branched, of more than 16 and up to 22 carbon atoms, but most have 18 corresponding to the stearyl residue. The main function of softener molecules, when applied to fabric, is that it adds on the surface, penetrate and provide an internal plasticization of the fibre forming polymer by reducing the glass transition temperature T_g . Thus, the physical arrangement of the softener molecules on the fibre surface is

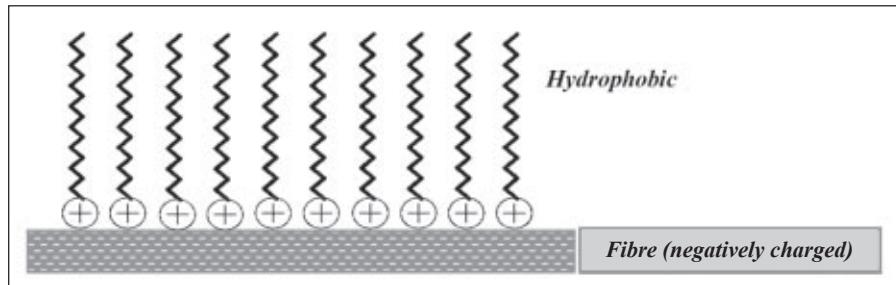


Fig 1 : Orientation of cationic softeners at textile surface

important which, in turn, depends on the ionic nature of the softener molecule and the relative hydrophobicity of the fibre surface. On the basis of chemical nature, softeners are classified as cationic, anionic or non-ionic^{3,4}. They are predominantly liquid dispersions with typical solid levels between 10-40%.

Cationic softeners

Cationic softeners are mostly widely used in the textile industry; these provide the best softness and are also reasonably durable to laundry. Cationic softeners orient themselves with their positively charged ends toward the partially negatively charged fibre (zeta potential) as shown in Fig 1, creating a new surface of hydrophobic carbon chains that provide the characteristic excellent softening and lubricity^{4,5}. On the other hand, they are non-compatible with anionic products, cause yellowing upon high temperature exposure and, due to its ionic nature, attracts soil. The different properties and functional groups are given in Table 1.

Anionic softeners

Anionic softeners were the first to be employed in the textile industries. They orient outward with their anionic charged groups repelled away from the

negatively charged fibre surface (Fig 2). This phenomenon enables them to form a hydration layer, offering better wettability and antistatic properties, but less softness than the cationic softeners^{6,7}.

They are represented by the common formula $RSO_3.M$ or $ROSO_3.M$ (where R = alkyl or aryl; M = Na, K)². In general, they are sulphated or sulphonated compounds, mainly used as lubricants for yarns or fibres, providing softness and pliability, stability in alkaline conditions and good resistance to yellowing. In addition, they are used as crease preventing agents in processing, sanforizing and raising, and as sizing additives. They have good compatibility for single bath application along with optical brightening agents. However, they are sensitive to metal ions present in the water and also electrolytes in the finishing bath; They are mainly applied by padding process, given their limited substantivity. They are often used for special applications, such as medical textiles, or in combination with anionic fluorescent brightening agents^{8,9}. The different properties and functional groups are given in Table 1.

Amphoteric softeners

Amphoteric softeners represent the

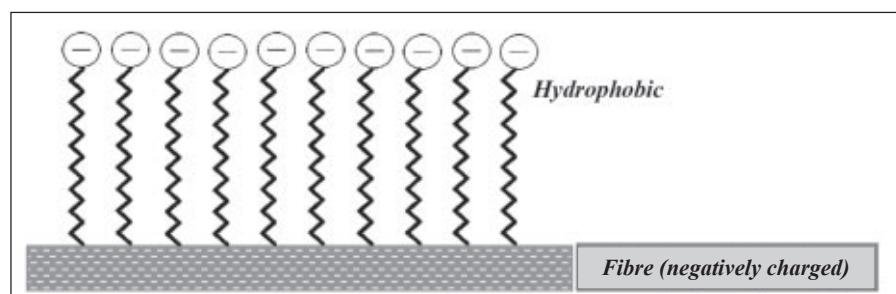


Fig 2 : Orientation of anionic softeners at textile surface

compound containing potentially anionic (carboxyl) and cationic (amine) groups within the same molecule, similar to amino acids and proteins. Typical properties are moderate softening effects, low permanence to wash and high antistatic effects because of their strong ionic character. Due to proteinic and biodegradable nature, they are recommended for white goods where antistatic and hydrophilic properties are expected^{1,8,10}. The characteristics and functional groups of the amphoteric softeners are given in *Table 1*.

Non-ionic softeners

Non-ionic softeners have the general formula $R(OC_2H_4)_nOH$ or $R(C_2H_4)_nOOH$ (where R = alkyl) and contain different non-ionic components such as fatty alcohols, ethoxylated fatty alcohols, ethoxylated fatty amines, paraffins and oxidized polyethylene waxes as active ingredients; theoretically, they have no electric charge and, for that reason, show no significant substantivity^{2,10}. They often require emulsifiers to produce stable dispersions. The non-ionic softeners chain orientation mainly depends upon the fibre surface nature; the hydrophilic portion gets attracted to hydrophilic surfaces, and the hydrophobic portion gets attracted to hydrophobic surfaces, as shown in *Fig 3*.

3. They are applied by different methods such as padding, spray or foaming applications, or exhaust processes, namely soft flow systems, yarn dyeing devices, winches or jigs. Additionally, in some commercial products, a combination of cationic and nonionic softeners is chosen to improve the solubility at lower temperatures. They are ideal for the finishing of optically-brightened white textiles due to good stability against high temperature and have almost non-yellowing characteristics¹¹.

Silicone softeners

In the current scenario, silicone softeners are the most extensively employed softeners in the textile industries. Silicones are macromolecules composed of a polymer backbone with alternating silicone and oxygen atoms with organic groups attached to the silicone molecules. They are described with the general formula R_2SiO (*Fig 4*); they are often identified as being polymeric. The effect comes from the siloxane backbones, its flexibility and its freedom of rotation along with Si-O bonds.

Currently, there are five generations of silicone softeners present in the market. They are non-reactive silicone,

amino modified silicone oil, polyether modified silicone oil, linear $(AB)_n$ block copolymers, and pyrogenic silicas. These softeners are supplied as aqueous emulsions, i.e. dispersing silicone oil in water using an appropriate emulsifier^{12,13}. The deposition of the softener on the fabric, the product stability and the performance of the silicone mainly depends upon the type of emulsifier, the particle size of the emulsion¹⁴, the hydrophilicity of the polymer, the nature of the functional groups, the extent of modification and the method of emulsification¹⁵.

Micro emulsions drop sizes are in the range of 50-150 nm; drop sizes between 150-300 nm are macro/normal emulsions. Micro emulsions provide better soft handle than normal ones, because they penetrate more inside the fibre bundle. In past decades, silicone manufacturing industries produced nano-emulsions with sizes around 10 nm; it has been determined that they impart an inner softness with a unique cool and dry handle to woven and knitted fabrics^{16,17,18}. The most important organic substituents used in the commercial silicones are methyl groups, the majority of which are polydimethyl siloxanes. A diversity of silicone technologies applications is available in textile industry applications; these include polydimethylsiloxanes, amido, amino functional silicones, methyl hydrogen silicones, epoxy functional silicones, hydroxy functional silicones, silicone polyethers and epoxy polyether silicones^{19,20}. The general functional properties of silicone softeners are given in *Table 1*. *Table 2* shows the silicone modification with different chemical groups and their properties.

Fibre-dye-softener interaction

The four types of softener can be used for fibres or textile substrates that have positive or negative groups, or are largely inert, such as polyester. The dyes used may get attached to these fibres by different forces, namely electrostatic forces, non-polar forces,

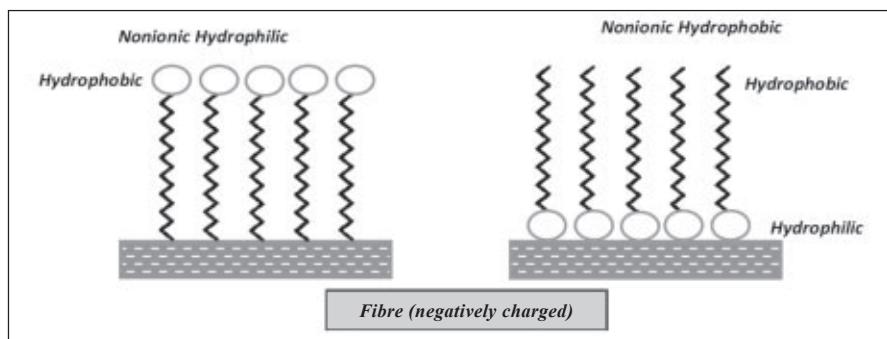


Fig 3 : Orientation of non-ionic softeners at textile surface

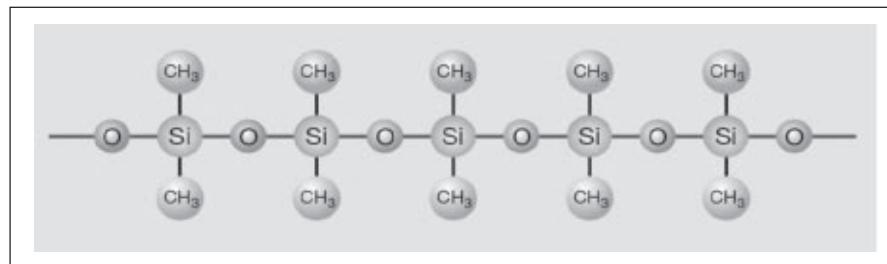


Fig 4 : Molecular structure of silicone

Table 1 : Properties of different types of softeners used in textile industry ^{21,22}					
Properties	Cationic	Anionic	Non-ionic	Amphoteric	Silicones
Softness	Best softening effect	Less softening effect than cationic types	Medium softening effect	Medium softening effect	Excellent softening effect
Durability	Durable to laundering	Easily washed-off	Not durable to dry cleaning	Low permanence to washing	Highly durable
Substantivity	High substantivity and can be applied to all types of fibres	Often used in special process, such as medical textiles	No ionic charge, no significant substantive effect	Better substantivity than anionic types	High substantivity
Compatibility	Non-compatible with anionic products	Good heat stability and compatible with other components of dye baths	Provides excellent compatibility in resin baths and easy to mix into a formulation	Shows good compatibility with anti-wrinkle finishes, flame retardants etc	High lubricity to the fibre owing to their low surface energy
Functionality	Provide a hydrophobic surface but poor rewetting properties	Provides strong antistatic effects and good rewetting properties	Minimal impact on fastness properties	Have no lubricity properties & good antistatic effect on especially white fabrics	Special unique hand, high lubricity, good sewability
Heat Stability	May cause yellowing upon exposure to high temperatures	Good yellowing resistant and good stability to alkaline conditions	Mostly resistant to yellowing (mainly for whites)	Medium stability to yellowing	Shows good stability to temperature and has good yellowing resistance
Functional groups	Amine salts, imidazolines, amino esters, fatty alcohol based, fatty acid and polyamine, dicyandiamidestearyl amine, Diethanolamine	Sulphated or sulfonated compounds	Polyethylenes, glycerides, ethoxylates, ethoxylated fatty alcohols and acids, paraffins and oxidized polyethylene	Betaine, substituted amino acids, sulphobetaine	Nonreactive, conventional reactive, organofunctional and amino functional silicones

dissolving effects and covalent bonds; the dyes can be anionic, cationic, non-ionic or fibre reactive. The application of surface-active chemicals can diminish the strength of the fibre-dye interaction or bond in many cases. Consequently, in considering the choice of a softener for a given fibre, the types of dye, ionic nature of softeners and the electric charges of fibres must be

considered^{23,2}. Table 3 shows the classification of textile softeners, according to their ionic nature.

Interaction is possible if the softener has the opposite charge as the dye. This will be apparent itself as a loss of fastness and colour. Softeners with the same charge as the dye will also result in less effect²³. Table 4 shows the fibre, dye, softener choice and remarks.

By theory, it is very clear that certain types of softeners should not be employed on certain fibres, e.g. cationic softeners on polyamides, but these still can be used to obtain the softness and other property requirements. In such circumstances, care is needed in the choice of softeners.

The major factor to be considered while handling cotton substrates is influence of pH and residual alkalinity. Residual alkalinity on cotton substrates can disturb the pH bath and create issues where finishes necessitate acid pH. Under alkaline condition, the cationic softeners will have less propensity to 'ionize' and thus leads to lower fixation onto the cotton fabric substrate. While applying cationic

Table 2 : Silicone modifications and their properties	
Silicone modifications	Properties derived
Amino group	Highly exhaustible and durable softness
Hydrophilic group	Water adsorptive
Methyl group	Water repellence and antistatic finish
Hydrogen group	Water repellence and soil resistance
Other organo modifications	Drapery and wrinkle recovery property

Table 3: Ionic nature and electric charge of softeners

Softener ionic nature	Electric charge
Quaternary groups	Positive, pH independent
Pseudo-cationic	Positive at pH < 7
Amphoteric	Weakly negative to weakly positive, depending on pH
Anionic	Negative
Non-ionic	No charge, neutral

softener in an exhaust bath, the speed of exhaustion of the cationic agent onto cotton fabric depends on the strength of the positive charge that it carries. This, in turn, depends on the pH. Cationic softeners carry relatively higher positive charge at lower pH (4-5) and, therefore, get exhausted more quickly even at cold conditions. The complete exhaustion takes place at pH 4-5. This high rate of exhaustion on cotton is also very undesirable, since it develops some uneven spots and stains on the fabric surface. Thus, the pH conditions need to be properly maintained for different softeners based on the temperature and MLR ratio. Also, fabric construction and geometry influence the ease or difficulty to softener penetrations. Overall, a weakly acidic condition is recommended by the manufacturer or supplier of the softeners to achieve

uniform and even exhaustion. Usually, the time of exhaustion required for the softeners will be 20-30 min. In case of cationic amino siloxanes function groups, the film formation of the siloxanes on the surface of the fabric and its reactivity with cellulose gets weakened, leading to inadequate feel. The durability to wash gets decreased because of absence of reactivity of the end hydroxyl group of the siloxane with 'OH' of cellulose due to pH disturbance. Overall, incomplete removal of anionic soaps and detergents normally used in the prior soaping operation results in precipitation of the softeners and thus lowers the softening effect. A proper rinsing cycle after soaping is to be given in order to minimize this problem.

At most times, dyers face yellowing issue after the softener finish. This

yellowing is mainly due to the cationic group of quaternary ammonium compounds, where the free hydrogen atom of amine group binds with the chlorine atom to form chloramines; this also results in fishy odour. But, quaternary ammonium compounds containing tertiary amines do not cause such type of yellowing, and thus can be used for whites. Non-ionic softeners are prone to show an adverse effect on wet and dry crock fastness properties due to thermo-migration²⁴. Softeners and lubricants make use of non-ionic emulsifiers based on nonylphenol ethoxylates and alkyl alcohol ethoxylates, which are responsible for bleeding of dyes and staining of the ground²⁵.

In case of modified silicones, such as amino silicones along with emulsifier, in acidic pH they behave cationically. On the other hand, they lose positive charge in an alkaline medium and cause aggregation and coalescence of silicone oil which results in stains on the fabric. Thus, the emulsion becomes unstable, and softness is lost. Another reason for silicone fabric staining is due to the fabric being passed through silicone emulsion with low cloud point emulsifiers, as the emulsion breaks up at these elevated temperatures. Hence,

Table 4 : Fibre, dyes, softener choices and remarks

Fibres	Charge	Common dyes	Softener type	Remarks
Acrylics	Negative	Acid dyes	Cationic	Result in very little colour change or loss in fastness. In addition, as the fibres contain anionic groups and the softener is cationic, good substantivity can be obtained
Nylon, wool, silk	Weakly negative (neutral)/ weakly positive (acidic)	Acid dyes	Cationic	Because acid dyes are employed on these fibres, the dye interaction must be carefully considered when choosing a cationic agent
Cellulosic	Negative	Direct dyes/ Anionic OBA	Anionic	Cationic softeners result in loss of brilliance and whiteness; colour changes on direct dyed goods often occur
		Vat, sulphur, reactive natural dyes	Cationic/ silicone	Care is required while selecting the softener; if the goods have poor absorbency properties, high temperature should be avoided (to avoid yellowing)
Polyester	No charge	Disperse dyes	Non-ionic	Not much softeners are used for polyester/ synthetic fibres. With increased interest in antistatic dressings on polyester softeners, specially designed antistatic agents are being investigated.
Cellulose acetate and triacetate	Weakly negative	Disperse dyes	Cationic and non-ionic softeners	

a proper choice of emulsifiers is important²⁶.

Methods of application

The application method of softener on to the textile substrate depends on the type of operation and machines available at the particular processing unit. In some cases, at soft flow processing unit where the fabric is exhaust dyed, the final softener may be exhausted onto the fabric at the end of the dye cycle. In most cases, the softener is applied on a separate machine, namely padding machine or at the final stenter machine stage, in open width form. In case of garment processing, the softeners are usually applied by exhaustion method.

Padding technique is perhaps the

best method of application of softeners. Since the amount of softener applied can be calculated accurately, with efficient machinery, a uniform application is ensured. Pad-dry or pad-dry-cure is the common methodology followed in the industries for knits in open width and woven fabrics. For tubular knit fabrics, the common methodology employed is balloon padding machine.

To achieve uniformity and trouble-free application, the following points need to be considered²⁵:

- Proper mixing of the emulsion, solution or dispersion of the softener
- Proper maintenance of the padding mangle
- Uniform moisture content of the fabric (especially in wet-on-wet process)
- Efficient rinsing of the fabric before

padding to avoid chemical or anionic carry over, especially when cationic products are used

- Adequate shear resistance of the emulsion
- Finally, uniform dyeing system is necessary to avoid migration of the softener.

Effectiveness of softeners

Traditionally, fabric softness has been evaluated by a qualitative hand measurement, which is a sensory judgement given by a group of panelists (subjective measurements). This methodology provides a general expression of people's reaction by touching a fabric, and the same is communicated to the respective fabric

Table 5 : List of plant based or bio-based textile softeners manufacturers and claims³¹⁻³⁶

Manufacturer	Base	Product name	Application	Claims
Archroma	Plant based	Siligen EH1	For both woven and knitted articles; can be applied by padding process as well as by exhaust process	35% plant-based active content; features ultralow cyclic siloxanes (D4, D5, D6)
Devan Chemicals	Vegetable oils	Passerelle Soft NTL	Natural fibres like hemp, cotton; also fit for synthetic fibres like rPES, PA etc	Wash durable & bio-content of the technology is above 85% (ASTM D6866-20)
Wacker	Plant based methanol	WETSOFT Eco 810LV, Wacker FINISH EcoWR 1100 LV FINISH LV EcoWR 1300 LV	810LV-Well suited for treating towels, underwear and t-shirts; WR1100 (synthetic or mixed fabrics) & 1300 LV (viscose or for natural fibres) - pants, shirts or table linen; padding as well as by exhaust process	Eco and fossil-based products differ only in the way that the methanol component is manufactured
Schutzen	Seeds of fruits	Schutzen BIOSOFT C90 & BIOSOFT-NIX	For cotton; especially excellent instant hydrophilicity for terry products	The working mechanism on textile articles is based on a novel 'Train-Loop-Tail' Technology
CHT Group	Recycled silicone & renewable bio-based emulsifiers	TUBINGAL RISE	Applied for all fibre types, apparel clothing sports textiles, outdoor clothing, home textiles	Recycled Innovative Silicone Emulsion, the world's first fabric softener made of more than 60% recycled and reprocessed silicone waste and renewable bio-based emulsifiers
Atlantic Care Chemicals	Sugarcane, bagasse, (agricultural waste)	Novosoft LV 90 Extra	All types of garments and textiles	It is a vegan, amphoteric charged and pre-hydrogenated softener concentrated paste; very smooth hand with high moisture absorption and anti-static properties.

manufacturers and consumers. Simple methods to measure some aspects of fabric hand were described by Dawes and Owen²⁷. Many factors such as the fabric colour, environmental lighting and its surroundings etc influence the physical evaluation of the fabric hand feel²⁸. The American Association of Textile Chemists and Colorists has published guidelines for subjective hand evaluation²⁹. One technique that has attempted to be more specific in giving an objective measure of hand is the Kawabata method. In this method, using regression technique, a relationship was established between the fabric mechanical properties, as measured by the KES-FB instruments and the fabric hand measurements, as subjectively graded by a Japanese expert panel. The regression equation was used to calculate the total fabric hand values. Although this test procedure is interesting from a scientific perspective, significant commercial acceptance is still not reached. Durability to washing of softening finishes can be evaluated by subjecting the finished fabrics to actual washing treatments using the parameters of AATCC Method 61 or the ISO 105C06 washing method, depending on the fabric type. Accelerated home laundering methods can be applied, followed by an evaluation of the retention of performance properties of the fabrics³⁰.

Sustainable developments

Textile is the second most polluting industry after the petrochemical industry. At textile clusters, there is an accumulation of large amounts of toxic sludge and dry toxic waste which is really no way of disposing of or handling in an ecofriendly way. Most water bodies like rivers, lakes and streams are totally contaminated by colours and other toxic chemicals. Millions of dyed garments are washed every day globally which result in heavy household effluents. During these washes, a small amount of chemicals leach in the sewage water system which, in turn, has destroyed the aquatic life and also

the domestic environmental ecosystem, overall leading to negative impact on the global front. Today, sustainability and green chemistry are the major topics in the textile industries. Majority of the buyers are very conscious in buying their clothes, garments, or any other form of textiles goods due to the environmental impacts. Many textile chemical manufacturers are moving out from the chemical based raw materials to greener and sustainable raw materials for the synthesis of various textile auxiliaries. Many of the manufacturers have started to introduce plant based/bio-based softeners in the market. Most of them are based on ester-qaut based chemistry along with natural plant vegetable oils. A list of few plant-based or bio-based softeners launched recently in the market and their respective product insights/claims are given in *Table 5*.

Simple methods for manufacturing softeners for household purposes²²

An ecofriendly and more economical alternative to the commercial fabric softeners can be made at home. The following are the simple methods which can be easily made:

Procedure 1: Essential oil and vinegar

Combine 3.8 l (0.8 gallon) of vinegar with 15 to 20 drops of essential oil which is available in local market such as lemongrass oil, cinnamon oil, lemon oil etc. Stir the essential oil directly into the container of vinegar for a minute in order to mix well. Here, vinegar is the component responsible for softening clothes and even acts as an antibacterial and antimicrobial agent. Add a few ml (1-2 teaspoon), depending upon the quantity of clothes before the dyer stage in the washing machine.

Procedure 2: Baking soda and salt recipe

Epsom salts or coarse sea salt and baking soda can be used for the formation of fabric softener in dry form, and the powder can be employed for during the home washing cycle to create a dry fabric softener that can be added into the washing machine. Use a

1/4 cup of baking soda for every full cup of Epsom salt. For every cup of Epsom salt, add 10 to 15 drops of essential oils and stir well until all of the essential oil has been spread over and absorbed by the salt. Add 2-3 tablespoons of this mixture directly into the washing cycle.

Procedure 3: Vinegar and baking soda

Take two cups of water; add half a cup of baking soda in it and stir well. Once mixed completely, add half of vinegar and few drops of essential oils, and mix the mixture completely. Use 1/4th of the mixture directly for the laundry in the washing machine.

Conclusion

Textile softening agents are of great importance for textile finishing and care. The continuing development of procedural method with new machines, fabrics and fibres, as well as new trends and rising consumer demands for quality, comfort and ecological will play a major role in the creation of revolutionary textile softener solutions. Moving towards the development of greener and ecofriendly softeners and the same, if employed globally, will reduce the environmental issues, mainly the carbon footprint and the water pollution.

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AD

Chemours unveils Ti-Pure Sustainability product series

Chemours, a global chemistry company with leading market positions in Titanium Technologies, Thermal & Specialized Solutions, and Advanced Performance Materials, recently announced a new Ti-Pure titanium dioxide (TiO_2) product portfolio: the Ti-Pure Sustainability (TS) series, which includes two high-performance grades. This new product family showcases Chemours' commitment to advancing its enterprise, business unit, and customers' sustainability goals.

'When we say we aspire to be the most sustainable TiO_2 enterprise in the world, we mean it,' says Ed Sparks, President, Titanium Technologies and Chemical Solutions at Chemours. 'Our customers are hungry for sustainable solutions, so we are proudly answering the call with both new and existing sustainably-minded TiO_2 innovations.'

The first two products in the new Ti-Pure Sustainability

series include:

- Ti-Pure TS-6300, a high-opacity pigment for coatings applications designed to advance sustainability, minimize climate impact, and maximize resource efficiency through superior hiding power and reduced material consumption. To help customers quantify the environmental impact reduction of this grade, Chemours recently launched the Ti-Pure TS-6300 Environmental Footprint Calculator.
- Ti-Pure TS-6200, a super durable grade specifically designed to advance sustainability, minimize climate impact, and maximize resource efficiency through improved dispersion and reduced energy, extended product life and avoided waste. Both are existing grades specifically designed to empower coatings formulators to create high-quality, long-lasting products that reduce material consumption and CO_2e emissions.