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Cosmetic properties and structure of fine-particle synthetic precipitated silicas

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Synopsis

Submicron-fine particle, synthetic silicas are of three types: fumed silicas, silica gels and precipitated silicas. Recent research has led to the synthesis of a wide variety of new controlled-structure, functional-precipitated silicas which exhibit unique cosmetic and dentifrice properties. The end-use applications of the precipitated silicas can be controlled by controlling their structure. It is now possible to make predictions regarding the thickening, viscosity building, humectant demand index, dentifrice abrasive and polishing characteristics of the new class of synthetic, precipitated products. The methods of preparation, the chemistry, the structure and the new cosmetic applications of the precipitated products are discussed.

I. INTRODUCTION

Fine-particle, synthetic silicas are amorphous, submicron size, white powders. In the literature, these products have often been referred to interchangeably as silicas, hydrated silicas, silicon dioxide, silicic acid, fillers, silica pigments, xerogels, aerogels, amorphous silicas, etc. The discussions which will be presented here will hopefully clarify and distinguish between the various types of silicas.

Silicas can be categorized into two major classes: natural silicas and synthetic silicas. Since the natural silicas are mined from the ground and are quite different in structure, properties and functions than the synthetic silicas, we have excluded these products from our discussion here.

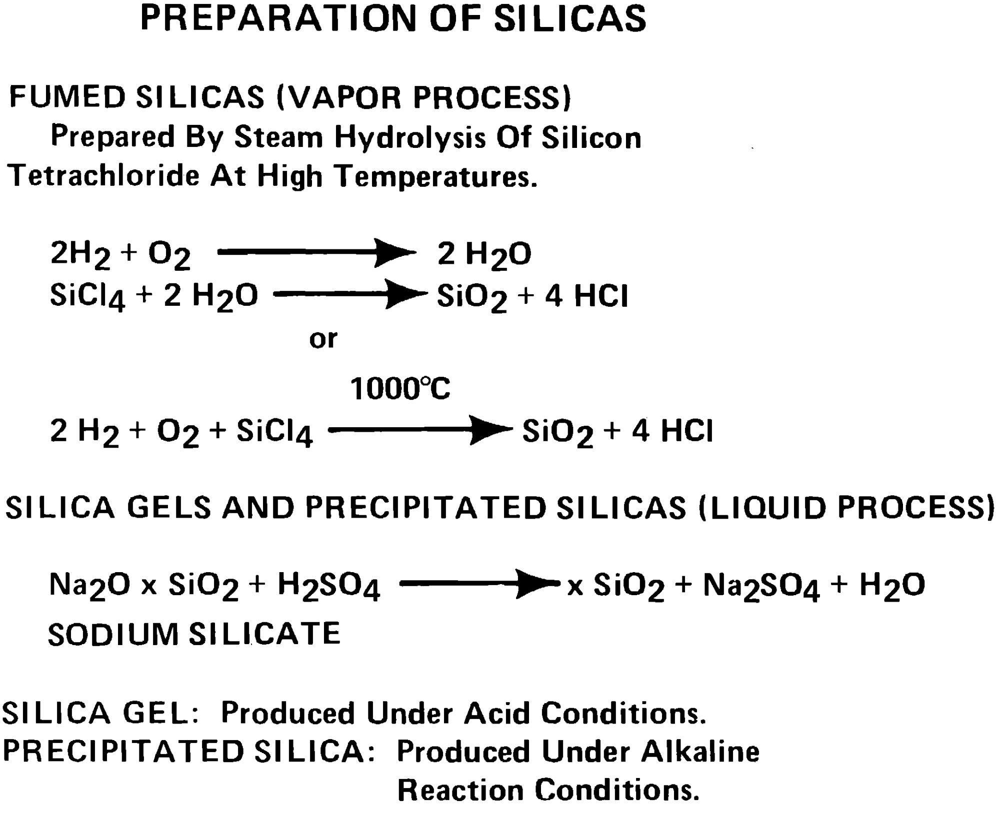
Synthetic silicas are of three types: fumed silicas, silica gels and precipitated silicas—and are prepared either by a vapor phase process or by a liquid phase process. Products which are synthesized by the vapor process are called fumed silicas. The products which are derived from the liquid process or wet process are further categorized as silica gels or precipitated silicas. In the CTFA (Cosmetic, Toiletry and Fragrance Association) cosmetic ingredient dictionary (1) the adopted name for the precipitated silicas and silica gels is hydrated silica; the fumed silicas are referred to as silicas.

For the present discussion we will first review the key properties of the three types of silicas. Then we will discuss the results of our recent research investigation in which we have learned more about the chemistry, structure and properties of the precipitated products. We have learned that the properties of the precipitated silicas can be fixed by controlling their structure during precipitation. We have synthesized precipitated silicas with diverse combinations of properties, and we will discuss how their silica structure can be correlated to key properties and functional performance.

II. OVERALL VIEW OF SYNTHETIC SILICAS

A. METHOD OF PREPARATION

As mentioned earlier, the known synthetic silicas are prepared either by the vapor phase or by the liquid phase process. *Fumed silicas* are prepared by the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen at an elevated temperature (2, 3). The reaction conditions are shown in Figure 1. *Silica gels and precipitated silicas* are prepared by the acidulation of aqueous sodium silicate solution (4) with an acidification agent, such as sulfuric acid (see Figure 1). In the case of silica gels, the reaction is generally conducted under acid conditions. The precipitated silicas are produced under alkaline reaction conditions.



PREPARATION OF SILICAS

FUMED SILICAS (VAPOR PROCESS)

Prepared By Steam Hydrolysis Of Silicon Tetrachloride At High Temperatures.

$$2H_2 + O_2 \longrightarrow 2\,H_2O$$

$$SiCl_4 + 2\,H_2O \longrightarrow SiO_2 + 4\,HCl$$

or

$$2\,H_2 + O_2 + SiCl_4 \xrightarrow{1000°C} SiO_2 + 4\,HCl$$

SILICA GELS AND PRECIPITATED SILICAS (LIQUID PROCESS)

$$\underset{\text{SODIUM SILICATE}}{Na_2O \times SiO_2} + H_2SO_4 \longrightarrow x\,SiO_2 + Na_2SO_4 + H_2O$$

SILICA GEL: Produced Under Acid Conditions.

PRECIPITATED SILICA: Produced Under Alkaline Reaction Conditions.

Figure 1. Preparation of silicas

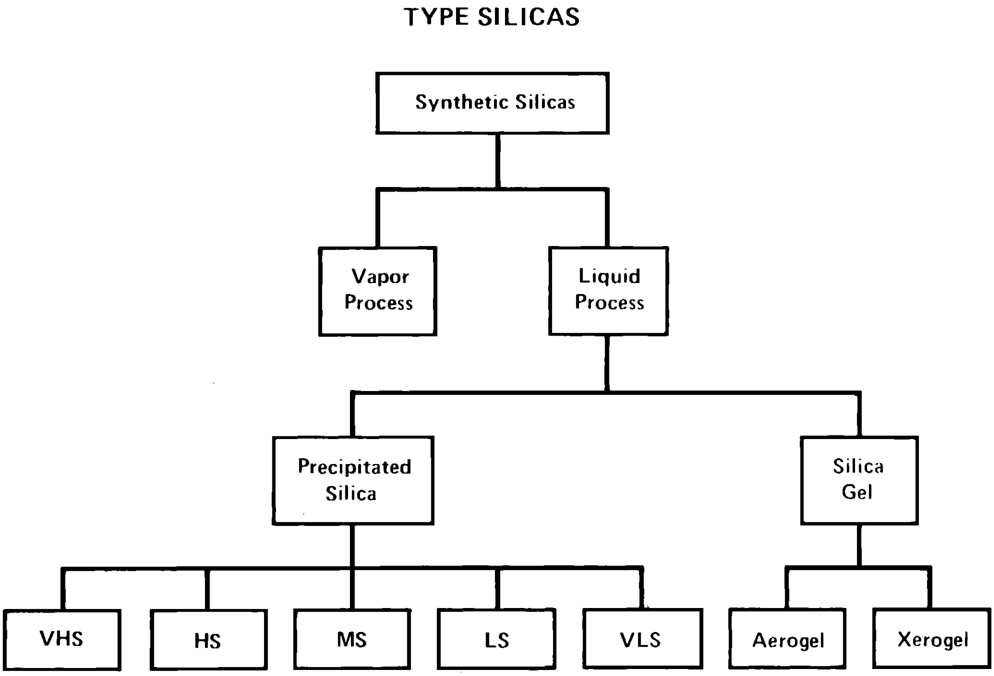


Figure 2. Type silicas

B. TYPES OF SILICAS

A system for classifying the various types of synthetic silicas is found in Figure 2. It is shown in Figure 2 that silica gels are of two types, xerogels and aerogels. During the manufacture of silica gels first a hydrosol, then a hydrogel is formed. When a hydrogel is washed and then dried from an organic medium without the shrinkage of structure (4), it is called an aerogel. Otherwise, it is called a xerogel.

Development of new, controlled-structure silicas has created the need for further classifying the precipitated silicas into five classes (see Figure 2): VHS—Very High Structure, HS—High Structure, MS—Medium Structure, LS—Low Structure and VLS—Very Low Structure.

The end-use properties of a precipitated silica are related to its structure, its particle size and its surface silanol group density. The definitions of the VHS to VLS are discussed later in the text under Section III-B.

C. COMPARATIVE PROPERTIES OF SYNTHETIC SILICAS

The properties of the fumed silicas (prepared via the vapor process) have been studied by many workers (5–7) and their properties have been found to be similar in some respects to the silicas prepared by the liquid phase or wet process. This is understandable in that the properties of the fine-particle synthetic silicas, regardless of their method of preparation, must be related to the following key parameters: BET surface area, particle size and silanol group density.

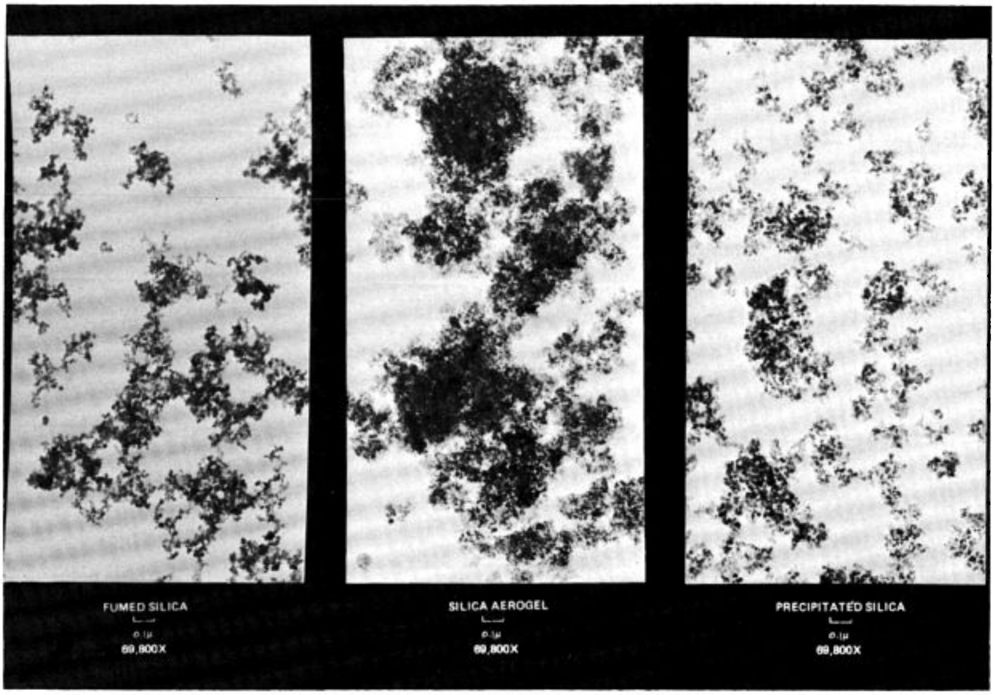


Figure 3. Electron photomicrographs of three types of synthetic silicas

From BET surface area measurement, one can calculate the primary particle diameter of synthetic silicas assuming spherical particles. In real life, these primary particles do not exist in the silica powder as such, but are further aggregated to exhibit the secondary particle structure (3). The secondary particles further aggregate during the manufacturing process to form the tertiary structure called the "agglomerates." Thus in synthetic silicas one can envision the following three types of particle size structure: primary particles (also called ultimate particles), secondary particles (also called aggregates) and tertiary particles (also called agglomerates). Primary particles are easy to recognize in fumed silicas and somewhat more difficult to recognize in precipitated silicas. The existence of primary particles in silica gels is purely hypothetical (8).

We have compared the electron micrographs of a typical fumed silica, a silica aerogel and a precipitated silica in Figure 3 at the same magnification of 69,800X. From the examination of Figure 3, one can clearly recognize the primary particles of the fumed silica. These primary particles exhibit a chain-type structure or secondary structure. In the electron micrograph of the precipitated silica one can recognize the primary structure in which the primary particles form irregular-shaped secondary structure of varying sizes.

In the electron micrograph of the typical silica aerogel one does not see the primary particles; instead, one sees a secondary, three dimensional mesh that is supposedly responsible for the very high internal surface area in silica gels (8).

In Table I we have listed the comparative physical properties of the three types of silicas. Silica gels exhibit very high BET surface area due to internal porosity. Fumed

Table I
Comparative Properties of Three Types of Silicas

PROPERTY	FUMED	SILICA GEL	PRECIPITATED
Surface Area (m^2/g)	200-400	300-1000	60-300
Type Surface Area	External	Internal	External
Porosity	Non-porous	Porous	Both
Bulk Density, g/l	32-64	96-160	160-192
5% pH	3-4.2	4-7.5	6.5-7.5
Silanol Groups/nm^2	2-4	4-8	8-10
Ave. Particle Diameter (nm)	14	--	18
% SiO_2 (Ignited Basis)	99.8 (Min.)	99.5	98.0

silicas and precipitated silicas exhibit relatively lower surface areas in comparison to the silica gels. Both the fumed silicas and precipitated silica are generally nonporous, but it is easy to create microporosity in the precipitated silicas during the process of manufacture.

The surface properties of synthetic silicas, such as viscosity building, thickening, adsorption and rheological properties, are related to the silanol group density of the silica surface and the extent of hydration. The surface properties of silica powders have been reviewed by Hockey (9) and Hair (10). It is generally recognized that there are three types (9, 11–13) of surface hydroxyl groups present on the surface of synthetic silicas: isolated, vicinal (on adjacent silicon atoms) and geminal (two silanols on same silicon atom) silanol groups.

The silanol group density is maximum in the precipitated silicas and eight to ten silanol group/nm^2 have been reported widely in the literature for the precipitated silicas. Since fumed silicas are prepared in a water-deficient reaction condition, it is not too surprising that they have extremely lower silanol group density/nm^2 than do precipitated silicas. It is believed that due to the very high reaction temperature used in the fumed silica process, initially almost all the silanol groups condense to form siloxane groups. But the presence of water vapor and lower temperature during the final stages of the manufacturing process result in rehydroxylation which increases the silanol group content in the fumed silicas to a final value of two to four OH group/nm^2.

Silica gels exhibit silanol group density intermediate between the extreme exhibited by the fumed and the precipitated silicas.

III. NEW CONTROLLED-STRUCTURE PRECIPITATED SILICAS

A. PROCESS VARIABLES

Precipitated silicas are produced by the acidulation of sodium silicate solutions with a mineral acid. The product properties can be controlled by controlling the key process variables. The key process variables and the manufacturing steps used in producing the precipitated silicas are depicted in Figure 4.

As an illustration, a low-structure precipitated silica is prepared (14 a, b, c) by first adding a fraction of the theoretical silicate needed for the reaction to a heated, stirred

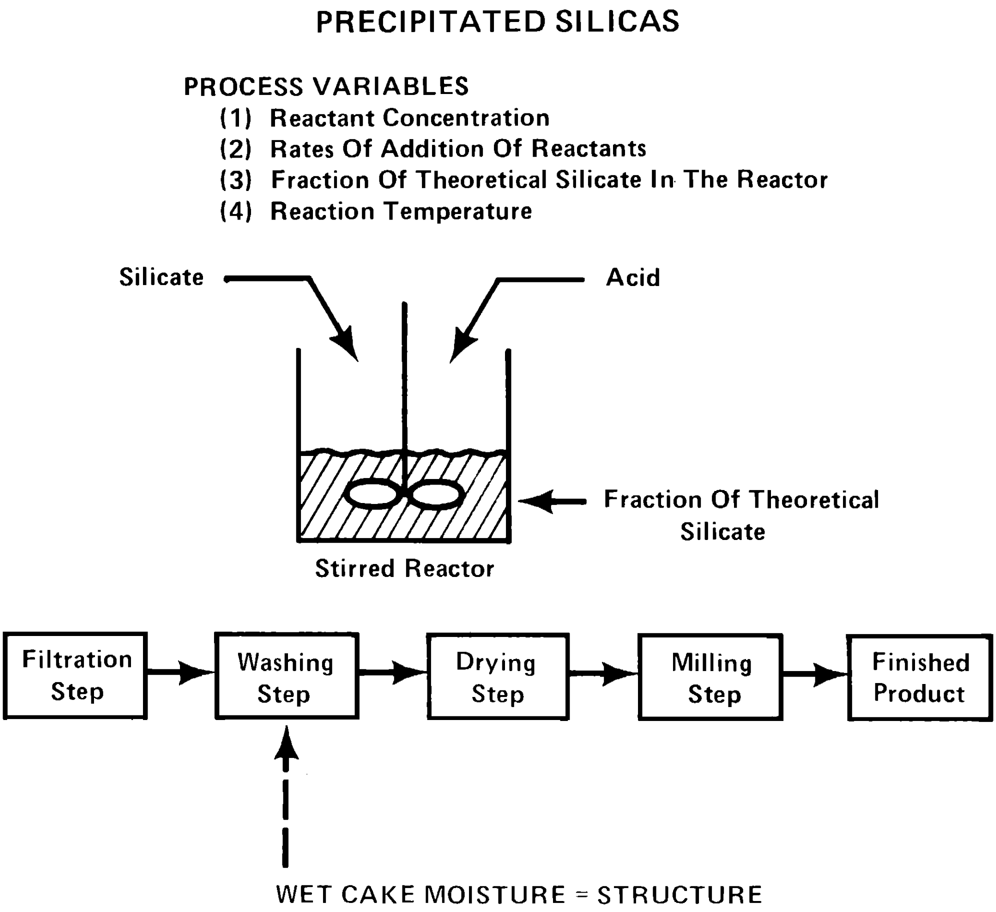


Figure 4. Precipitated silica manufacturing steps

reactor and then simultaneously adding the acidulating agent and the remaining silicate at predetermined rates until the silica precipitation is completed. At this point the precipitate is filtered, washed to remove the sodium sulfate by-product, dried and milled to the desired degree of fineness.

It turns out that the amount of water associated with the washed silica precipitate is the structural water, and it is a very important property which "tags" the product properties of the resulting dry finished product. This property is referred to as the % wet cake moisture (WCM). Under a given set of manufacturing and process conditions, % WCM will vary with the structure level of the dry product. A product with a very high % WCM content is defined as a high-structure silica and a product with a relatively low water content is defined as a low-structure silica. In this context, we will use % WCM or structure synonymously.

B. WET CAKE MOISTURE VERSUS STRUCTURE INDEX

As mentioned above, the water content of the precipitated product prior to drying is an important property. This water is present between the particles and inside the parti-

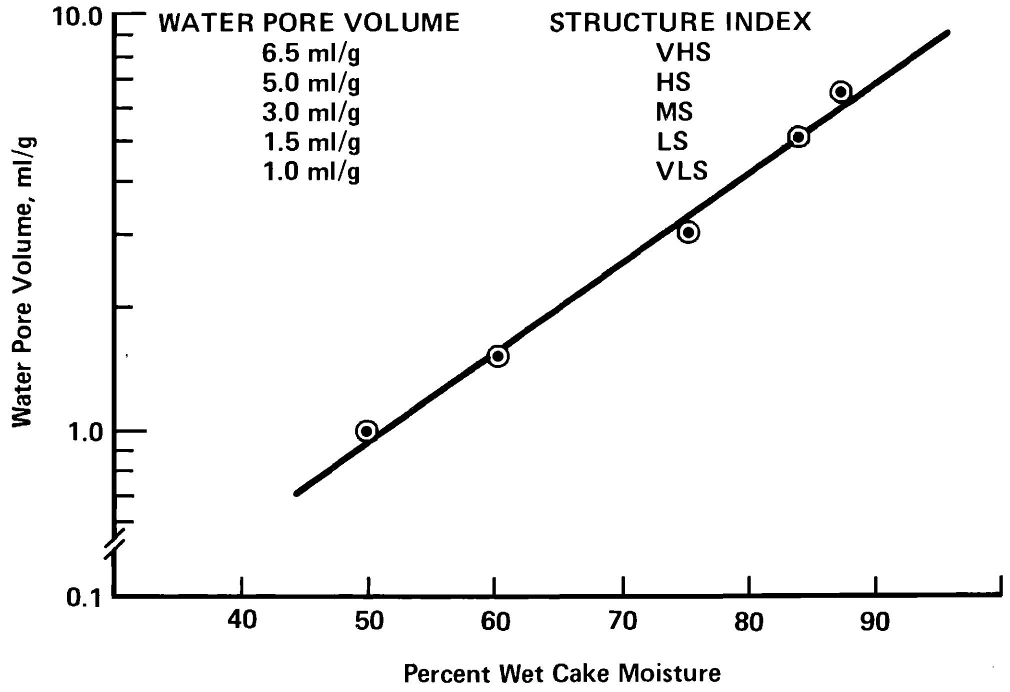


Figure 5. Plot of water pore volume versus WET cake moisture

cles. Therefore, at a fixed set of reaction conditions, the water associated with the precipitate or the filter cake is called the structural water. The amount of water associated with one part of the dry, recoverable product is defined as the water pore volume. The amount of water associated with 100 parts of the dry recoverable product is defined as Structure Index (SI) (15 a, b). Thus the water pore volume (PV) and SI are related to the % WCM by the following equation.

$$PV = \left(\frac{\%\,WCM}{100 - \%\,WCM}\right) \tag{1}$$

$$SI = \left(\frac{\%\,WCM}{100 - \%\,WCM}\right) \times 100 \tag{2}$$

A plot of water pore volume versus the % WCM is shown in Figure 5. Thus a product with water pore volume above 6.5 or SI values above 650 is arbitrarily defined as a VHS (very high structure silica). A low structure silica (LS) is one which exhibits a water pore volume above 1.5 or SI values above 150. These definitions are clearly explained in Figure 5. It must be pointed out that the log of the water pore volume or the log SI is linearly related to the % WCM. The SI values of products between the % WCM values of 80 to 85 are given in Table II (15).

C. STRUCTURE CONTROL

One of the key variables which can be used for controlling the properties and the structure of silica is the fraction of the theoretical silicate which is added to the reaction me-

Table II
WET Cake Moisture (WCM) Versus Structure Index (SI)

% WCM	SI
80	400.0
81	426.3
82	455.5
83	488.2
84	525.0
85	566.7

dium prior to the acidulation. Figure 6 shows how the silica structure increases as the fraction of the theoretical silicate in the reaction medium increases.

D. ELECTRON PHOTOMICROGRAPHS OF CONTROLLED STRUCTURE SILICAS

The electron photomicrographs of VHS (very high structure) and HS (high structure) silicas are shown in Figure 7. The comparative photomicrographs of MS (medium structure) and LS (low structure) silicas are shown in Figure 8. In Table III we have compared the particle size of the VHS to LS silicas. Examination of Table III clearly points to the fact that the primary particle size increases as the silica structure level decreases. Thus the control of particle size via controlling the silica structure provides an important tool for producing silicas for diverse specialty and cosmetic applications.

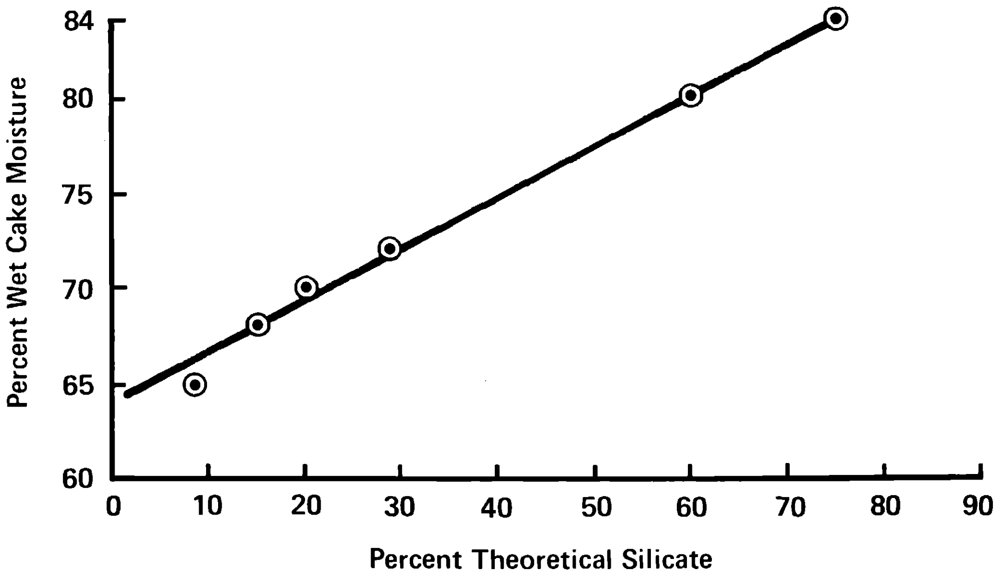


Figure 6. Method of controlling the silica structure

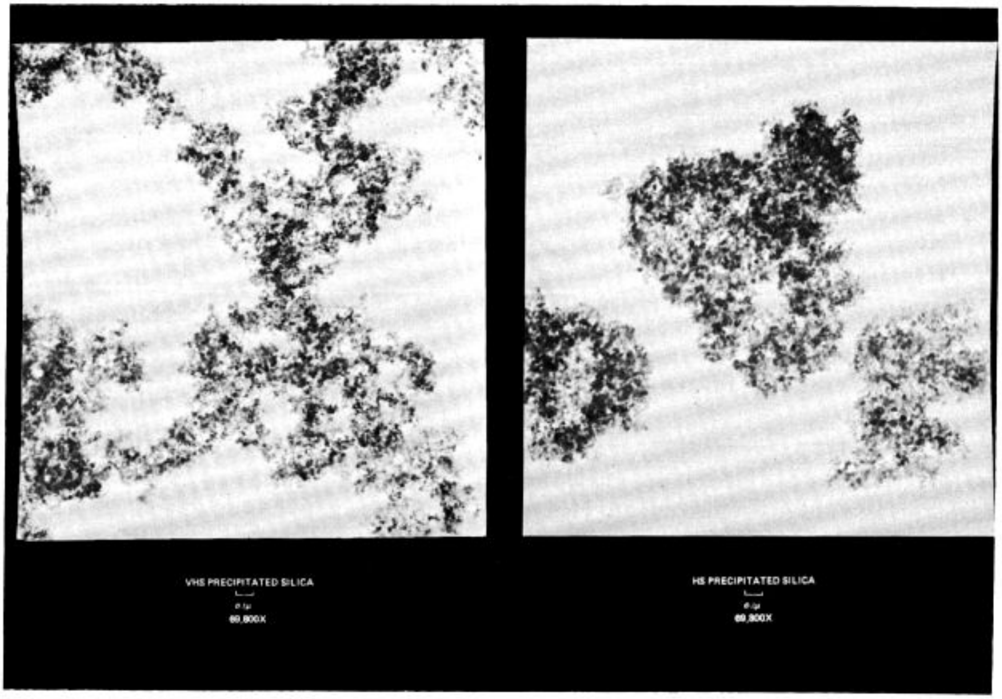


Figure 7. Electron photomicrographs of VHS and HS silicas

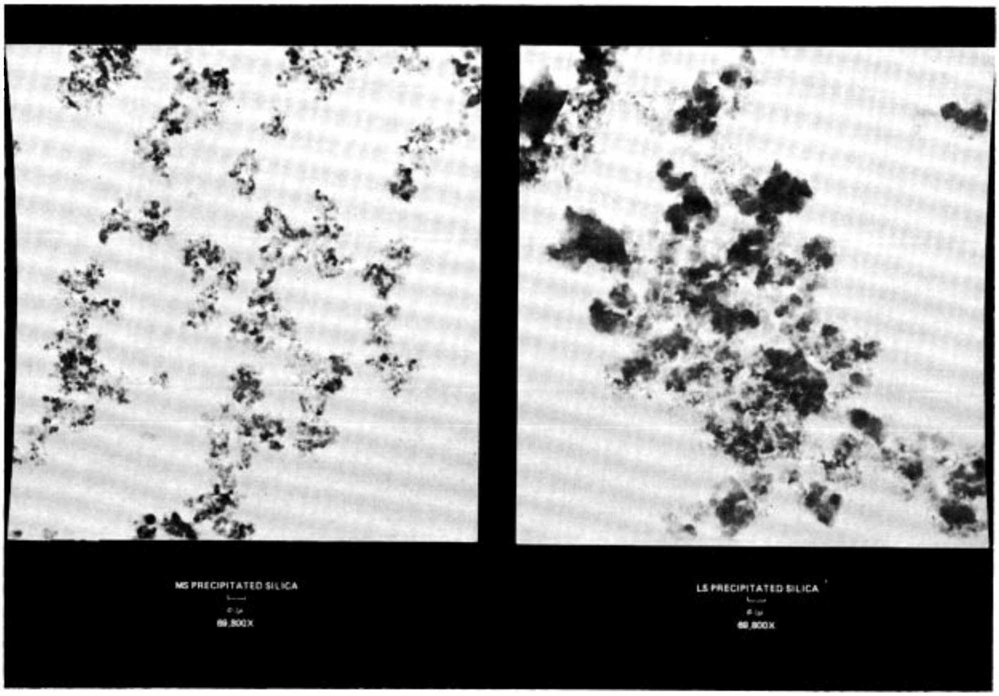


Figure 8. Electron photomicrographs of MS and LS silicas

Table III
Particle Size of Precipitated Silicas

		PARTICLE DIAMETERS, nm		
STRUCTURE	EMSA m^2/g	MEAN PARTICLE DIAMETER	MINIMUM	MAXIMUM
VHS	250	12	5	20
HS	175	17	5	30
MS	145	20	5	25
LS	60	51	5	300

IV. RESULTS AND DISCUSSIONS

A. METHOD OF EVALUATION AND PROPERTIES OF PRECIPITATED SILICAS

Six controlled-structure silicas (structure level from VHS to VLS) were prepared similar to the method illustrated in Figure 6. All the precipitated samples were washed, dried and air micronized to produce micron-size silicas. These six samples were designated as A, B, C, D, E and F. The finished samples were characterized by the various physical properties, such as oil absorption (OA), glycerine absorption (GA), mineral oil absorption (MA), sorbitol absorption (SA), BET surface area (BET), average particle size (APS), porosity by mercury intrusion (HGI), glycerine demand index (GDI), mineral oil demand index (MDI), sorbitol demand index (SDI), % wet cake moisture (WCM) and structure index (SI). The data are summarized in Tables IV and V. The oil absorption of silicas was determined by the ASTM rub-out method (16). This test is based on the principle of mixing linseed oil with a silica by rubbing with a spatula on a smooth surface until a stiff putty-like paste is formed. By measuring the quantity of oil required to produce a very stiff, putty-like paste, which will not break or separate when it is cut with the spatula, one can measure the oil absorption of silica—a value which represents the volume of oil required per unit weight of silica to saturate the silica sorptive capacity. The oil absorption value is calculated by the following eq 3.

$$\text{Oil Absorption} = \frac{\text{ml oil absorption} \times 100}{\text{weight of silica sample, gram}} \tag{3}$$

$$= \text{ml oil/100 g silica}$$

The ASTM method was modified in that the linseed oil was replaced by glycerine, mineral oil (saybolt viscosity 340 to 350) or sorbitol (70% solution) when running the respective humectant and mineral oil absorption values.

Surface area was determined by the nitrogen adsorption method (17) of Brunauer, Emmett and Teller (BET) while the average particle size (secondary particle size) was determined by the Coulter Counter method (18) using Model TAII.

The void volume of silicas was determined by the Aminco-Winslow Porosimeter (19). This instrument is a completely hydraulic machine used to measure the void structure of various materials. The mercury is forced into the voids as a function of pressure and the volume of mercury intruded per gram of sample is calculated at each pressure setting. Increments in volume (cc/g) at each pressure setting are plotted against the void size corresponding to the pressure setting increments. We have listed in Table IV the total intruded volume of mercury in cc Hg/g of silica.

Table IV
Properties of Precipitated Controlled Structure Silica Samples (A-F)

PROPERTIES/PRODUCT	A	B	C	D	E	F
STRUCTURE CODE	VHS	HS	MS	MS	LS	VLS
% WET CAKE MOISTURE	86	84	80	75	60	55
STRUCTURE INDEX	614.3	525.0	400.0	300.0	150.0	122.0
OIL ABSORPTION, ml/100g	210	196	177	153	92	72
GLYCERINE ABSORPTION, ml/100g	163	140	136	119	113	72
SORBITOL ABSORPTION, ml/100g	196	189	158	148	120	75
MINERAL OIL ABSORPTION, ml/100g	205	199	175	161	99	90
BET SURFACE AREA, m^2/g	200	140	125	85	65	50
AVG. PARTICLE DIAMETER, μm	3.0	3.2	4.2	6.4	8.0	9.6
MERCURY INTRUSION POROSITY, ccHg/g	6.32	5.39	4.66	3.94	1.84	1.58

Glycerine demand index (GDI), mineral oil demand index (MDI) and sorbitol demand index (SDI) values (listed in Table V) were determined by converting the respective liquid into free-flowing powders by the addition of silica for ease of handling and blending into dry formulations. Silica was mixed with a known weight of liquid until a free-flowing powder was obtained. The humectant demand index (HDI) or the drying-up capacity was calculated as the weight of the liquid dried up by 100 g of silica until a free-flowing powder was obtained.

The % WCM values of the precipitated silicas were determined by drying 100 g of the washed precipitate or the filter cake at 150°C until a constant weight of dry silica was obtained. The % WCM value is obtained by subtracting the dry weight of silica from 100 (the gross weight of the precipitate).

The SI values were calculated by using eq 2.

B. CORRELATION OF PROPERTIES VERSUS SILICA STRUCTURE

The experimental data listed in Tables IV and V were evaluated by a computer program using multilinear regression eq 4

$$\bar{Y} = \sum_{i=1}^{n} a_i \bar{x}_i + b \qquad (4)$$

where $\bar{Y}$ is the dependent variable such as % WCM or SI, $\bar{x}$ the independent variable and "a" is a multilinear regression coefficient.

Table V
Humectant Demand Index (Drying-up Capacity) Versus Precipitated Silica Structure

PROPERTY/PRODUCT	A	B	C	D	E	F
% WET CAKE MOISTURE	86	84	80	75	60	55
STRUCTURE INDEX	614.3	525.0	400.0	300.0	150.0	122.0
STRUCTURE CODE	VHS	HS	MS	MS	LS	VLS
GLYCERINE DEMAND INDEX, g/100g	265.0	242.5	233.3	212.5	100.0	92.1
MINERAL OIL DEMAND INDEX, g/100g	233.3	203.0	194.1	150.0	81.8	73.3
SORBITOL DEMAND INDEX, g/100g	257.1	244.8	233.3	185.7	98.0	88.7

Table VI
Correlations Between Precipitated Silica Structure (% WCM and SI) and its Physical Properties

STRUCTURE PARAMETER	PROPERTIES	CORRELATION COEFFICIENT	STRUCTURE PARAMETER	PROPERTIES	CORRELATION COEFFICIENT
% WCM	OIL ABSORPTION	0.998	LOG STRUCTURE INDEX	OIL ABSORPTION	0.999
	GLYCERINE ABSORPTION	0.920		GLYCERINE ABSORPTION	0.925
	SORBITOL ABSORPTION	0.967		SORBITOL ABSORPTION	0.970
	MINERAL OIL ABSORPTION	0.996		MINERAL OIL ABSORPTION	0.997
	BET SURFACE AREA	0.895		BET SURFACE AREA	0.926
	AVG. PARTICLE DIAMETER	0.981		AVG. PARTICLE DIAMETER	0.986
	MERCURY INTRUSION POROSITY	0.985		MERCURY INTRUSION POROSITY	0.995
	GLYCERINE DEMAND INDEX	0.991		GLYCERINE DEMAND INDEX	0.984
	MINERAL OIL DEMAND INDEX	0.986		MINERAL OIL DEMAND INDEX	0.993
	SORBITOL DEMAND INDEX	0.993		SORBITOL DEMAND INDEX	0.992

The calculations were carried out by the computer in which a correlation matrix is determined first. Then the program introduces the independent variable one by one. In step one, the variable $\bar{x}$ is introduced which has the strongest correlation with $\overline{Y}$. At each consecutive step the independent variable is introduced by the program which has the best correlation coefficient. Table VI gives the correlation coefficient results when the silica % WCM and log structure index (dependent variables) were correlated with the various physical properties listed in Tables IV and V. Note in Table VI that the % WCM and log structure index parameters of silicas correlate very well with the physical properties of silicas samples A through F. The various mathematical equations relating the silica structure with its physical properties are listed in Table VII. These equations suggest that there is a very high degree of correlations between the silica structure and its physical properties.

C. OIL ABSORPTION VERSUS STRUCTURE INDEX

The structure (% WCM) of silica correlates very well with the oil absorption. Therefore the oil absorption value can be used for predicting the end-use properties of the precipitated silicas. A plot of log SI versus oil absorption is shown in Figure 9.

Table VII
Mathematical Relationship Between the Precipitated Silica Structure and Its Physical Properties

% WCM (SILICA STRUCTURE) = 0.23 (OIL ABSORPTION) + 39.0
LOG SI (STRUCTURE INDEX) = 0.012 (OIL ABSORPTION) + 3.93

% WCM (SILICA STRUCTURE) = 0.38 (GLYCERINE ABSORPTION) + 25.7
LOG SI (STRUCTURE INDEX) = 0.019 (GLYCERINE ABSORPTION) + 3.24

% WCM (SILICA STRUCTURE) 0.26 (MINERAL OIL ABSORPTION) + 33.0
LOG SI (STRUCTURE INDEX) = 0.013 (MINERAL OIL ABSORPTION) + 3.63

%WCM (SILICA STRUCTURE) = 0.28 (SORBITOL ABSORPTION) + 32.4
LOG SI (STRUCTURE INDEX) = 0.014 (SORBITOL ABSORPTION) + 3.59

% WCM (STRUCTURE) = 0.21 (SURFACE AREA) + 50.3
LOG SI (STRUCTURE INDEX) = 0.011 (SURFACE AREA) + 4.47

% WCM (STRUCTURE) = -4.7 (AVG. PARTICLE SIZE) + 100.1
LOG SI (STRUCTURE INDEX) = -0.24 (AVG. PARTICLE SIZE) + 7.08

% WCM (STRUCTURE) = 6.7 (MERCURY INTRUSION POROSITY) + 47.0
LOG SI (STRUCTURE INDEX) = 0.34 (MERCURY INTRUSION POROSITY) + 4.33

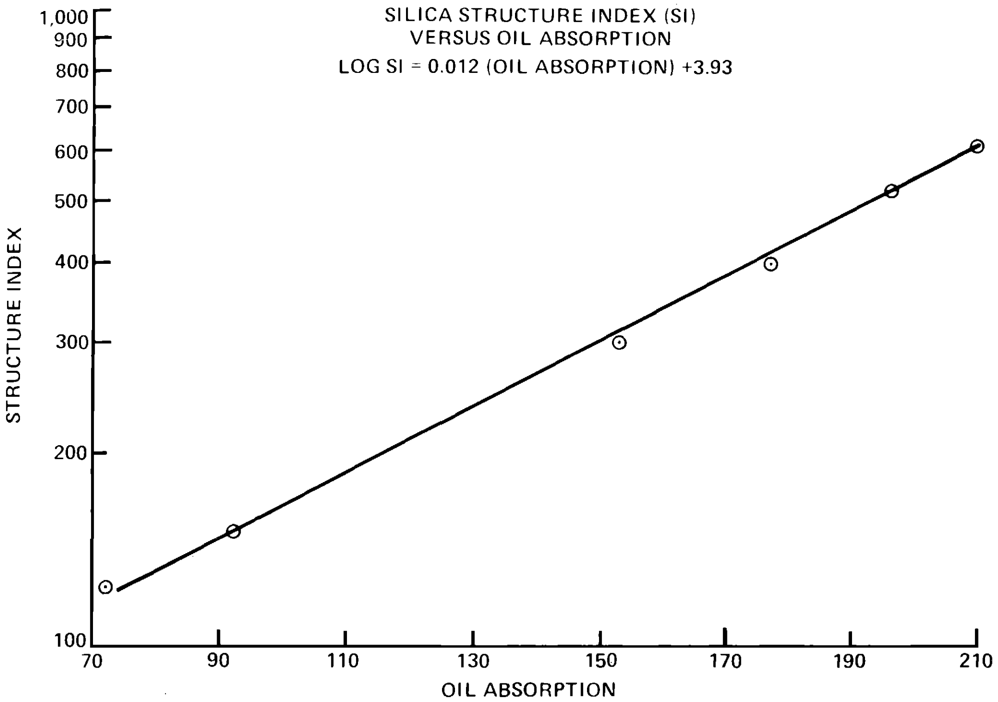


Figure 9. Plot of silica structure versus oil absorption

Experience of producing a wide variety of precipitated silicas has led us to the conclusion that VHS silicas exhibit oil absorption values above 200 ml oil/100 g silicas. The precipitated silicas between the oil absorption range of 125 to 175 ml/100 g silica are classified as MS silicas. Products with oil values below 200 and above 175 are called HS silicas. Products below 75 ml oil/100 g silica are called VLS silicas and the LS silicas range between the values 75 to 125 ml oil/100 g silica. Note that in Table IV we have referred to the product "C" as MS silica due to its WCM and SI values even though its oil absorption is slightly above the 175 ml oil/100 g silica cut-off range for the MS structure silica.

D. GLYCERINE, MINERAL OIL AND SORBITOL ABSORPTION VERSUS THE SILICA STRUCTURE

Figure 10 shows the relationship between the % WCM of silica samples and their corresponding mineral oil absorptions. Figure 11 is a plot of log SI versus the humectant absorption values of the various controlled-structure silicas. The mineral oil absorption values are relatively higher than the glycerine/sorbitol absorptions obtained with the same silica samples (see Table IV). This may be due to the nonhydrogen-bonding nature of the mineral oil. Note, also that the sorbitol absorption values are higher than the corresponding glycerine absorption values. The mathematical relationships between the silica structure and various liquid absorption values are predicted by the regression program. These equations are listed in Table VII as well as in Figures 10 and 11.

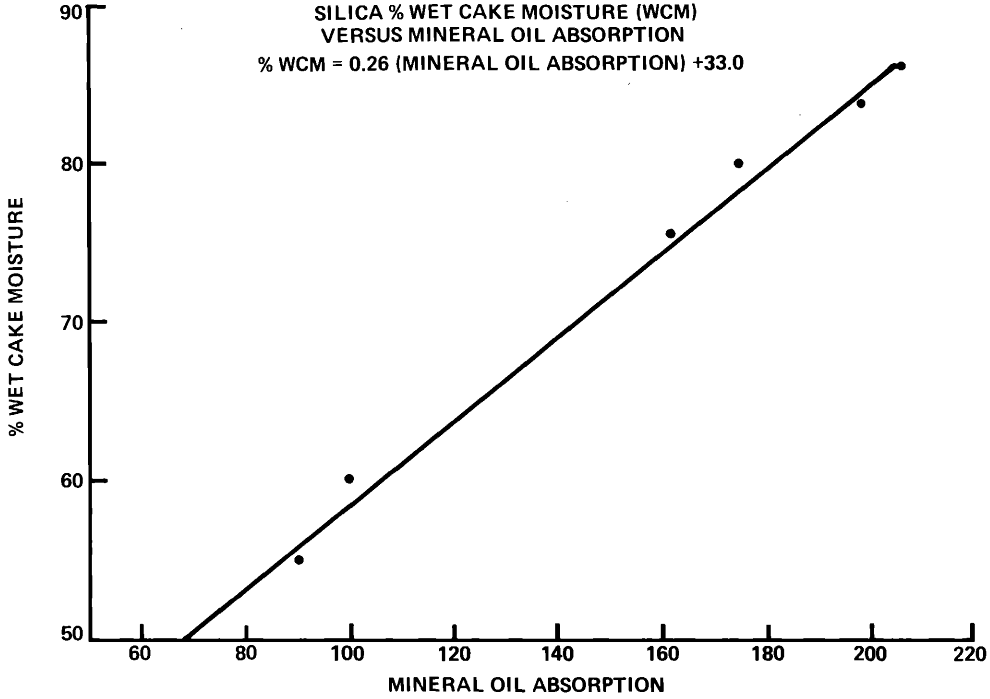


Figure 10. Plot of silica structure versus mineral oil absorption

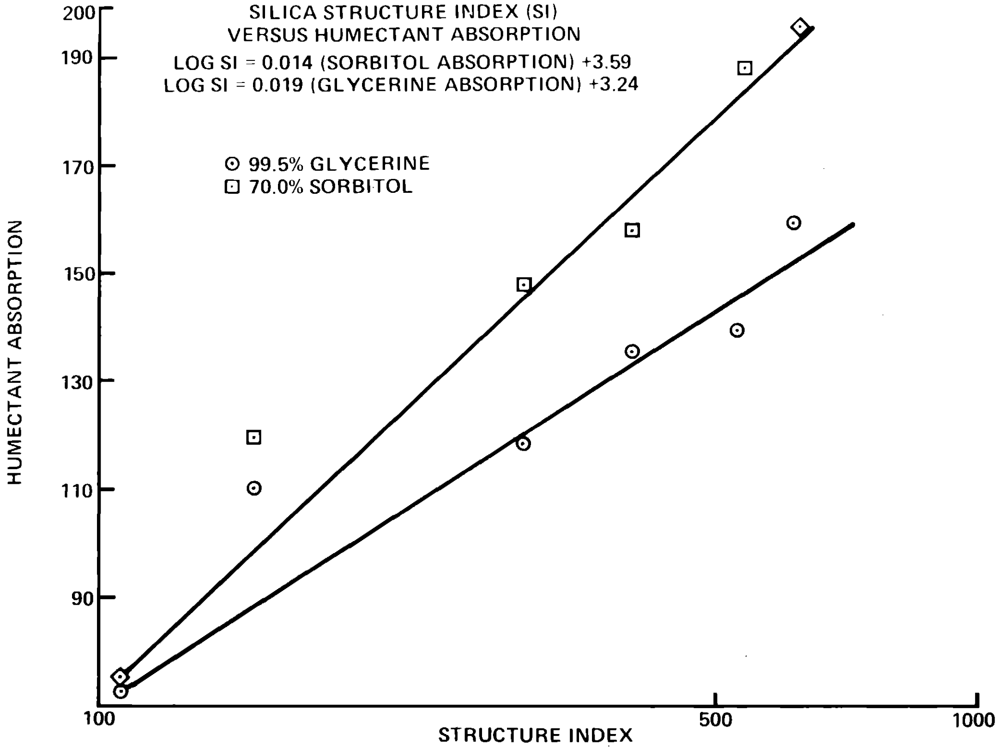


Figure 11. Plot of silica structure versus humectant absorption

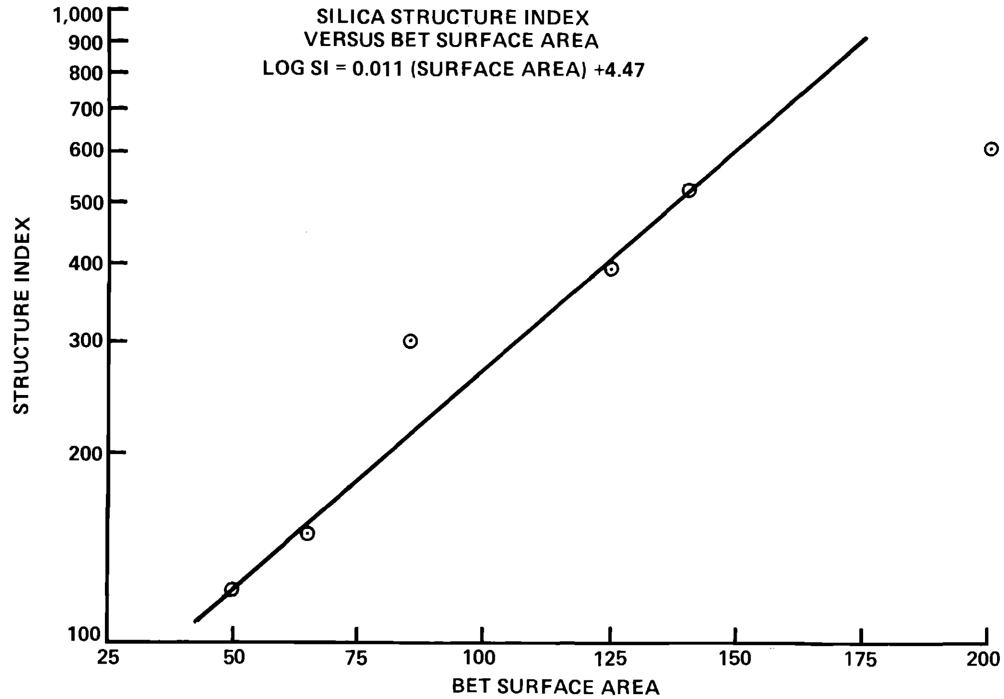


Figure 12. Plot of structure index versus BET surface area

E. SILICA STRUCTURE VERSUS THE BET SURFACE AREA

The BET surface area of the various controlled-structure silicas was correlated with the silica structure. A plot of log SI versus the BET surface area of the six controlled-structure silicas of Table IV is depicted in Figure 12.

F. AVERAGE PARTICLE SIZE VERSUS THE SILICA STRUCTURE

A good correlation was obtained between the various structurally different silica samples and their corresponding average particle size (secondary particle size). A plot of % WCM and APS (average particle size) is shown in Figure 13. Thus it is clear that as the silica structure decreases, the particle size correspondingly increases (see also Tables IV and VII).

G. VOID VOLUME VERSUS THE SILICA STRUCTURE

The relationship between the void volume of silica as determined by the mercury intrusion method and its silica structure is shown in Figure 14. A low-structure silica exhibits low-void volume and as the silica structure increases, the void volume of silica correspondingly increases. This is shown mathematically by regression equations in Table VII as well as in Figure 14.

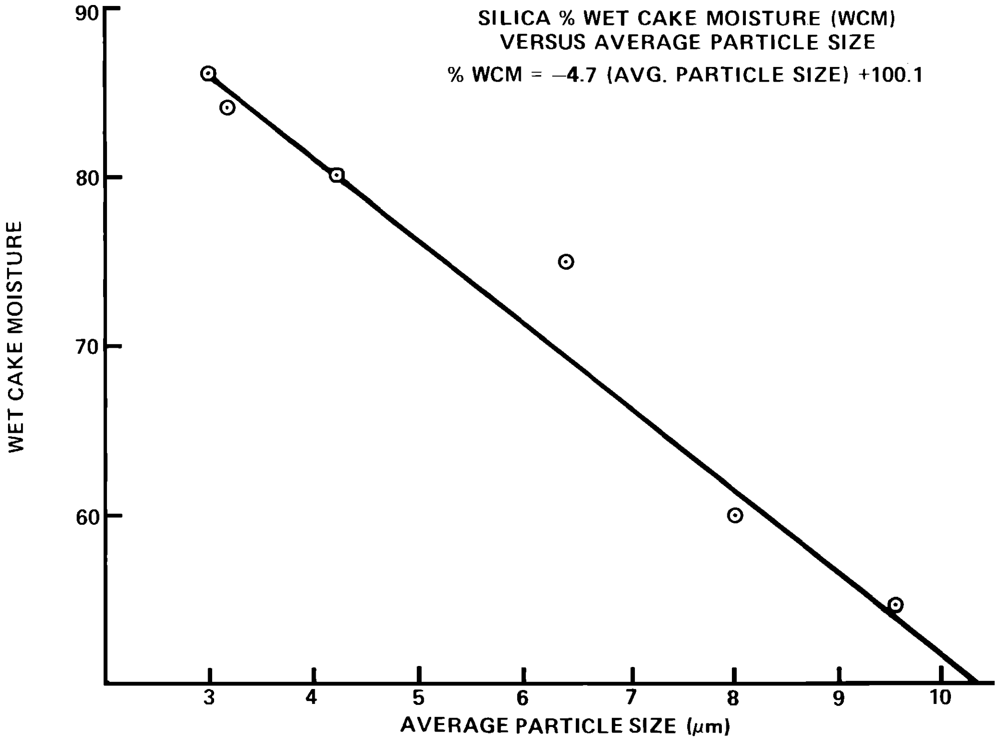


Figure 13. Plot of silica structure versus average particle size

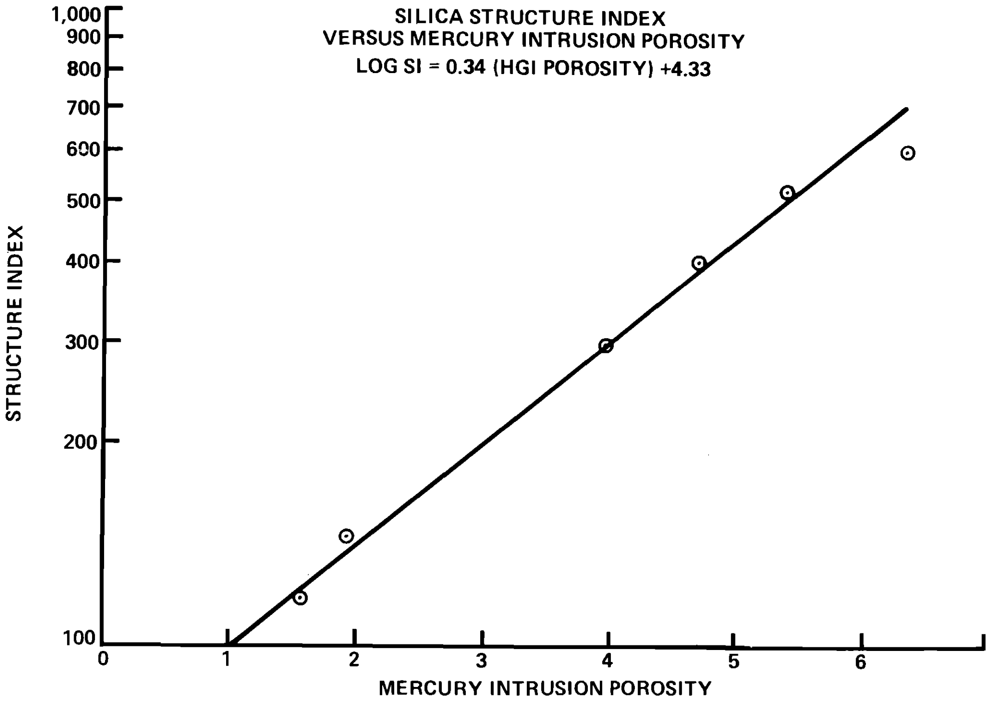


Figure 14. Plot of silica structure versus mercury intrusion porosity

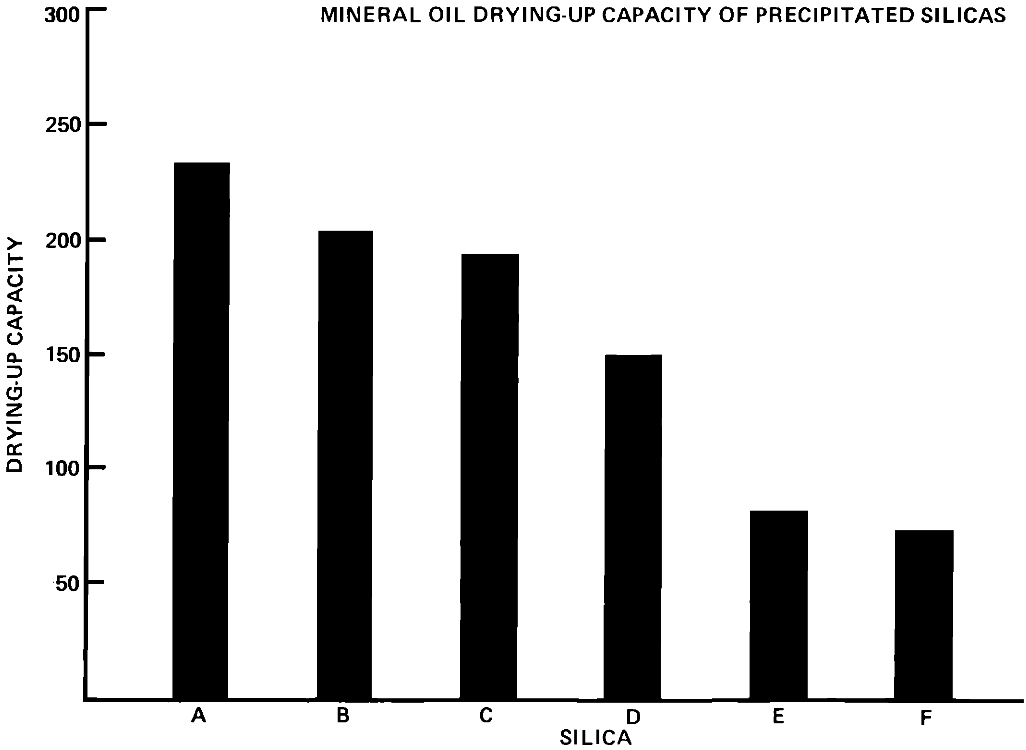


Figure 15. Mineral oil drying-up capacity of precipitated silicas

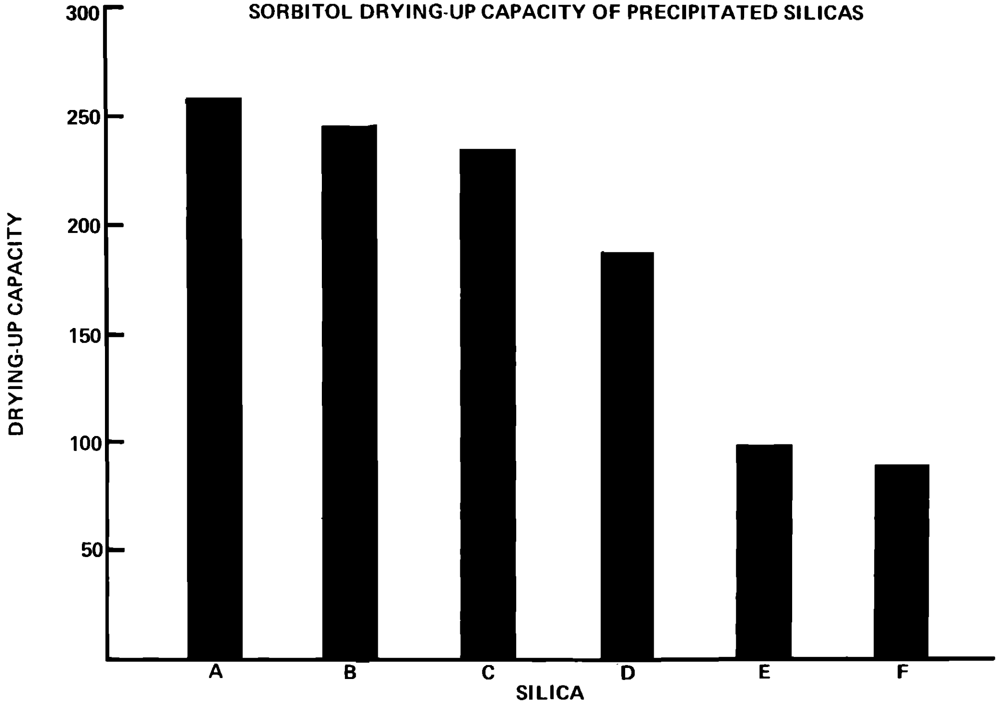


Figure 16. Sorbitol drying-up capacity of precipitated silicas

H. GLYCERINE, SORBITOL AND MINERAL OIL DEMAND INDEX VERSUS SILICA STRUCTURE

Precipitated silicas are used for converting the liquids into dry, free-flowing powders. This technique is used for ease of handling and dry blending "liquids" into many formulations. The drying-up capacity of precipitated silicas increases with the increase in the silica structure level. This is shown in Figures 15–17 and data are listed in Table V.

V. DENTIFRICE PROPERTIES OF CONTROLLED-STRUCTURE PRECIPITATED SILICAS

A. THICKENING AND VISCOSITY BUILDING PROPERTIES

The thickening and viscosity building properties of the six controlled-structure silica samples (for physical properties of silica, see Table IV) were studied in a nonhydrogen-bonding liquid (mineral oil), as well as a hydrogen-bonding liquid, such as glycerine (poly functional alcohol). The effect of silica concentration on the viscosity of mineral oil and glycerine is shown in Figures 18 and 19, respectively.

The thickening and viscosity building properties of the precipitated silicas are influenced by the following factors: 1) nature of the liquid medium, 2) structure of the precipitated silica, 3) concentration of the silica, 4) particle size and surface area of the silica, 5) silanol group density, 6) degree of dispersion, 7) nature of additives, if any, and 8) pH of the system.

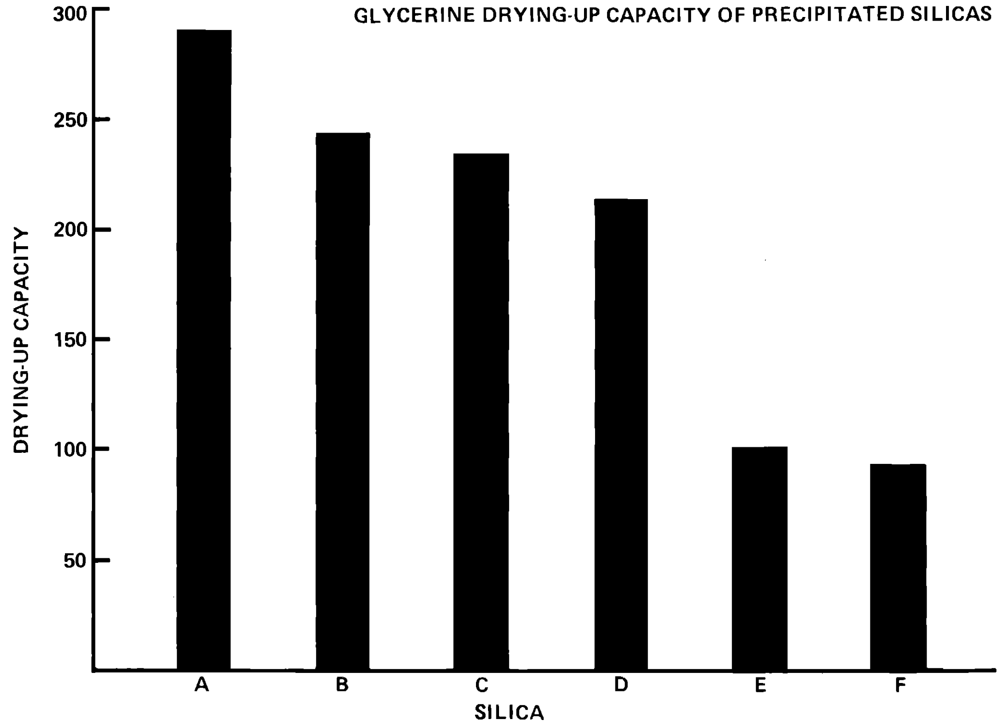


Figure 17. Glycerine drying-up capacity of precipitated silicas

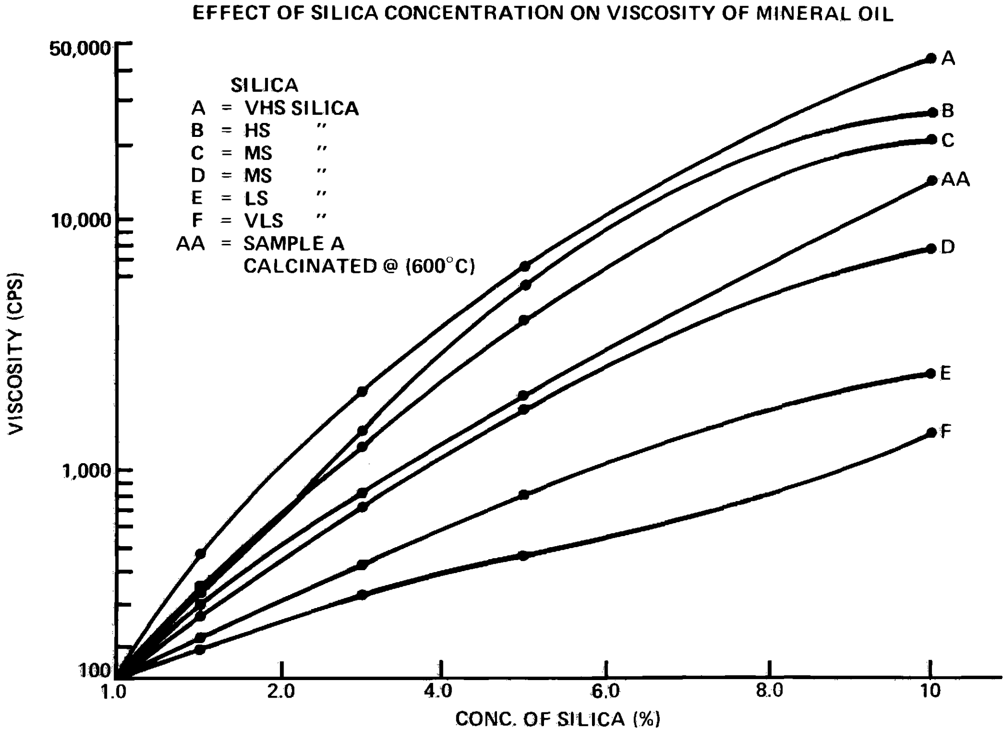


Figure 18. Effect of silica concentration on viscosity of mineral oil

From Figure 18, it is clear that only 3 to 6% of VHS silica (Sample A) is extremely effective in increasing the viscosity of mineral oil. At the same level of concentration (3 to 6%) the viscosity increase produced by the VHS silica (Sample A) is much lower in the glycerine medium.

This result is explained by the fact that the precipitated silicas produce a much higher viscosity increase when added to the nonhydrogen-bonding liquid system (mineral oil). In the nonhydrogen-bonding systems, the hydroxyl groups of the precipitated silicas have a greater tendency to hydrogen bond with each other because there is no competition for hydrogen bonding in the liquid medium. This situation is reversed when the silica is added to a hydrogen-bonding liquid system such as glycerine. The hydrogen-bonding liquid system competes for the silanol group of silicas thereby reducing the ability of the silica-silanol groups to hydrogen bond with each other. This explains the lower viscosity increase observed when silicas are added to the hydrogen-bonding liquid system.

The viscosity of a liquid system would increase when the silica structure level increases, the particle size decreases, the BET surface area increases and the silica concentration or use level increases.

It appears that the silanol group density of silicas also influences the viscosity of liquid systems. To prove this concept, a VHS silica, Sample A, was calcined for 2 hr at 600°C to partially remove the silanol groups. This calcined silica material, AA, was added to mineral oil to study the viscosity effects. From Figure 18, it is clear that the viscosity increase contributed by Sample AA (calcined VHS silica) is much lower than the vis-

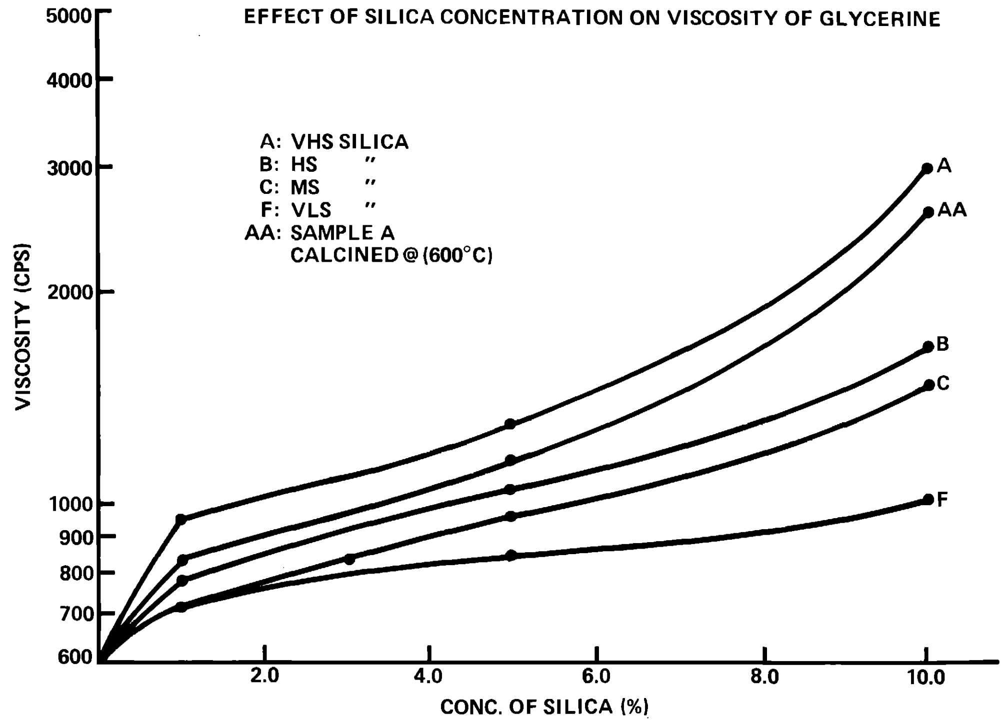


Figure 19. Effect of silica concentration on viscosity of glycerine

cosity increase obtained with the regular Sample A. This substantiates the fact that silica thickener efficiency is reduced when silanol groups are partially removed.

Additives have an effect on the viscosity behavior of silicas in various systems. In general, addition of 1 to 2% by weight (based on total weight of system) of a hydrogen-bonding additive (ethylene glycol, amines, etc.) to precipitated silica in a nonhydrogen-bonding or slightly polar system will increase viscosity because addition of the additive will increase the probability of silanol—silanol group interactions by acting as bridging groups. Large addition of additives (5 to 10%) of hydrogen-bonding additive would tend to decrease the viscosity of nonhydrogen-bonding, liquid-silica system.

It has been observed that the most favorable pH range for thickening liquid systems capable of hydrogen bonding is between 4 to 8; the maximum viscosity is obtained with silica close to pH 7.

In summarizing, for cosmetic applications one needs to choose a very high structure silica with the highest BET surface area and the finest particle size to obtain the maximum viscosity increase in a given system.

B. DENTIFRICE SILICA ABRASIVES VERSUS RDA

Dentifrice compositions contain an abrasive, liquid humectant, thickener, sudsing agent, flavor and minor amounts of other optional ingredients. Extensive studies have been undertaken by many workers concerning the cleaning, polishing and abrasivity of dentifrices. It is generally recognized in the literature that abrasivity and cleaning properties are more or less directly related, i.e., the higher the abrasivity, the greater the cleaning efficiency (20, 21).

It is well recognized that a dentifrice should contain some abrasive agent (21–23), but there has been concern expressed over the possible deleterious effects of excessive abrasiveness (20, 24, 25). The Council on Dental Therapeutics (24) cautions that a dentifrice should be no more abrasive than is necessary to keep teeth free of accessible plaque, debris and superficial stain.

We have undertaken extensive research and developed methods by which we can control the abrasivity of precipitated silicas (14, 15). Ideally, dentifrice abrasive should provide maximum cleaning and polishing with minimum abrasion to enamel, dentin and cementum. To do an effective job in a dentifrice, we believe the silica abrasive should exhibit the following properties: lowest humectant demand, controlled abrasivity, controlled particle size and shape, good fluoride compatibility, good cleaning properties and acceptable surface properties and compatibility behavior.

In a series of tests, we have found that low-structure precipitated silicas can be used effectively in dentifrices to provide an acceptable cleaning at low abrasion. The RDA (26) (radioactive dentin abrasion) of precipitated silica abrasives is related to silica structure (15). A plot of silica abrasive RDA versus its oil absorption is shown in Figure 20.

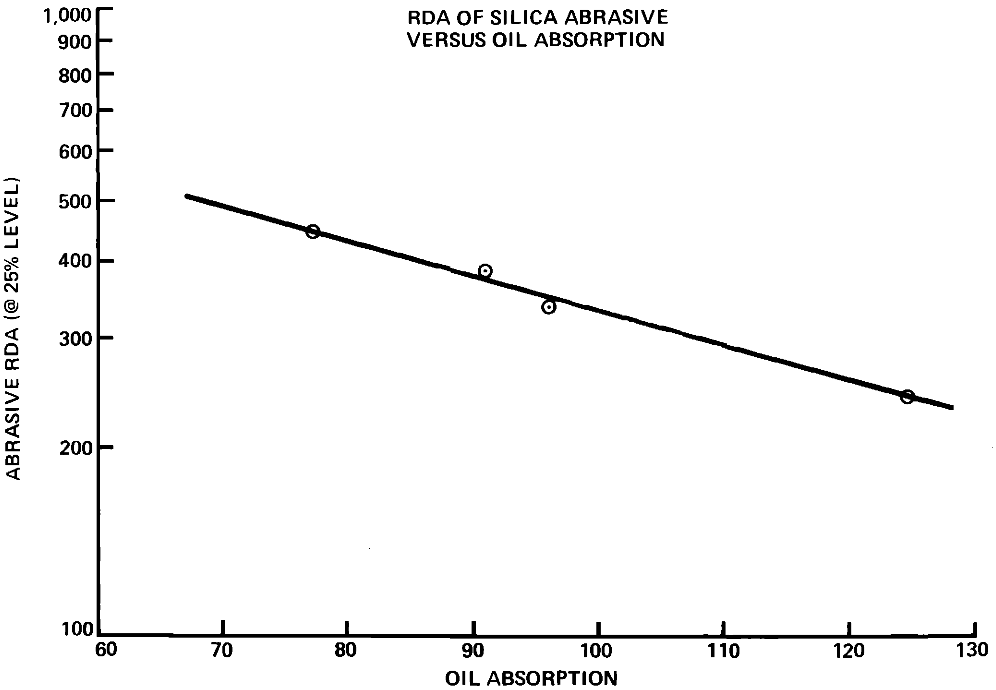


Figure 20. Plot of silica RDA versus oil absorption

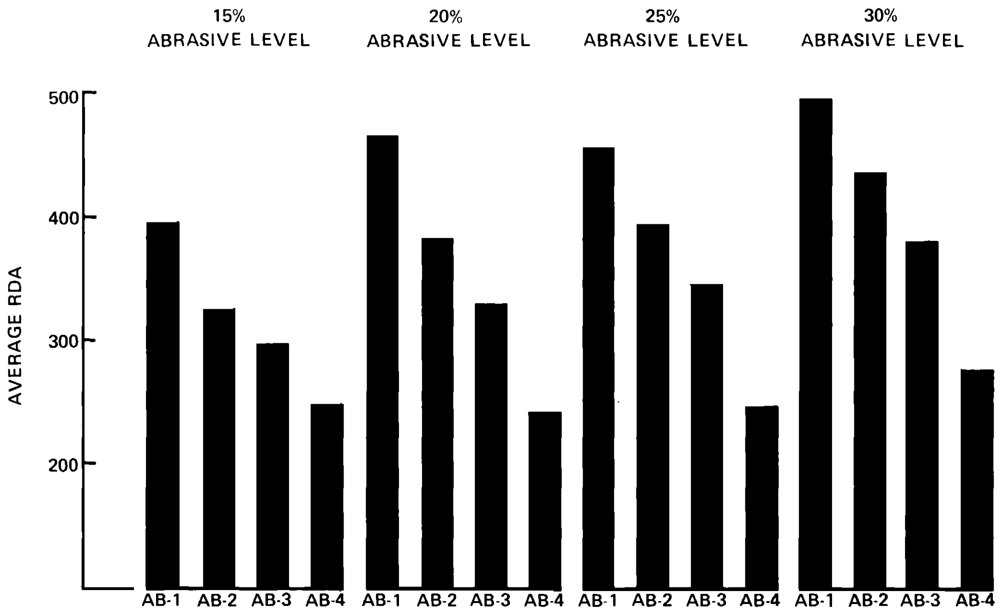


Figure 21. Effect of silica concentration on RDA

C. RDA VERSUS ABRASIVE LEVEL

A series of low-structure precipitated silica abrasives was prepared and evaluated for RDA at various levels of concentration. Figure 21 shows the effect of silica concentration on its RDA values; silica abrasive can be used at about 25% level in a dentifrice matrix to produce the acceptable RDA values. The RDA values of silica abrasives do not proportionately increase with the abrasive level. This gives the cosmetic chemist tremendous flexibility in formulating an acceptable dentifrice by controlling the level of silica abrasive in the dentifrice formulation.

The RDA of precipitated silica abrasive can be calculated by using eq 5

$$\text{RDA} = -4.17\,(\text{Oil Absorption}) + 5.3\,(\%\ \text{Abrasive Level}) + 640.8 \qquad (5)$$

VI. COSMETIC APPLICATIONS

The synthetic silicas are inert, nontoxic, chemically pure, white powders which are acceptable under the FDA regulations for use in food and cosmetic formulations. Typical properties of synthetic silicas are listed in Table VIII and are discussed below.

A. DRYING-UP LIQUIDS

For many food, cosmetic and pharmaceutical applications it is essential to dry up the active ingredients on an inert, nontoxic carrier. Synthetic silicas are widely used in such applications for drying up liquids into powders. Since the drying-up capacity of silica is related to its structure, a cosmetic chemist should choose a VHS or HS silica for this type of application.

Table VIII
Cosmetic Application of Silicas

PROPERTY	APPLICATION	SILICA STRUCTURE
DRYING-UP LIQUIDS	FOODS, COSMETICS, PHARMACEUTICALS	VHS, HS
ANTI-CAKING	FOODS, COSMETICS, HOUSEHOLD PRODUCTS	VHS, HS
CONDITIONING AGENT	PERSONAL CARE, SPECIALTY	VHS
SUSPENSION	HAIR CARE, DEODORANTS, COSMETICS, LIQUIDS	VHS
THICKENING	TOOTHPASTE, LIQUIDS, SPECIALTY	VHS, MS
TABLETTING AID	PHARMACEUTICALS, COSMETICS	VHS, MS
ABRASIVES AND POLISHING AGENT	TOOTHPASTE	LS, VLS
ADSORBENT	POLYOLS	LS, VLS
VISCOSITY CONTROL	NAIL POLISHES, COSMETICS	VHS
GLOSS REDUCTION	SPECIALTY	VHS, MS

B. ANTI-CAKING

Many cosmetic, food and pharmaceutical preparations tend to cake up in the container or the box in which they are packaged. Due to the fine particle size and very high absorption capacity of VHS or HS silica, these silicas are widely used to make cosmetic and specialty formulations free-flowing.

C. CONDITIONING

Some cosmetic and specialty powder formulations are difficult to flow due to moisture pick-up by one or several ingredients of the formulations. The flow properties and angle of repose of these powder formulations can be improved in such situations by the addition of 1 to 2% by weight of synthetic silica.

D. SUSPENSION AID

In many cosmetic formulations, such as in aerosol and antiperspirant formulations, a very small amount of silica is needed to provide suspension characteristics to the active ingredients of the formulation. A VHS or HS silica of high absorption capacity and surface area is used in this type of application.

E. THICKENING AGENT

The addition of 6 to 16% VHS or HS silicas to dentifrice formulations, aqueous or oil systems, would convert them to gels or pastes. The superior thickening efficiency of a precipitated silica depends upon its structure, particle size, surface area and nature of additives.

F. TABLETTING AID

Precipitated silicas serve as binders, eliminate sticking and act as tabletting aids in pharmaceutical and specialty applications.

G. ABRASIVE AND POLISHING AGENT

Due to mild abrasivity and controlled structure, precipitated silicas are used as mild abrasives and polishing agents in toothpaste formulations. LS and VLS silicas are ideally used because of their low humectant demand and acceptable compatibility features with other toothpaste formula ingredients.

H. ADSORBENT

Controlled-structure precipitated silicas are used to purify polyols and to remove traces of impurities from many liquids and effluents. The choice of proper silica would depend upon the nature and concentration of the impurity present in the liquid.

I. VISCOSITY CONTROL

A relatively small amount of VHS silicas increases the viscosity of creams, lotions, ointments, acne preparations and other specialty products enabling the cosmetic chemist to control the viscosity characteristics of his finished product.

J. GLOSS REDUCTION

Synthetic silicas are widely used as de-lustering agents to reduce the gloss of varnishes, lacquers and other surface coatings.

VII. CONCLUSIONS

We have presented here the structure, chemistry and preparation of controlled-structure precipitated silicas. We have correlated the properties and the end-use applications of silicas to their structure. The variety of cosmetic applications in which synthetic silicas are currently being used is already phenomenal. Further insight into surface chemistry and silica structure is needed to further explore the future cosmetic properties of synthetic silicas.

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