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by George C. Derringer
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Non-black reinforcers and fillers for rubber

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Commercial development of the rubber industry through the first two decades of this century depended heavily on non-black pigments, many still prevalent today (Fig. 1). Clay, whiting, zinc oxide, barytes, oxides of iron and lead, and many more such materials were used; materials readily available naturally or as by-products of other industries were candidates as rubber fillers.

The tire industry was born on non-black pigments, and, until World War I, zinc oxide and iron oxide were two of its major fillers. The success of the first carbon blacks in greatly improving rubber properties introduced the age of reinforcement. With this came the quest for fillers having small particle size.

Early efforts were directed to reducing the particle size of zinc oxide. In the early 30's precipitated calcium carbonates became available, first in relatively coarse particle size and later in the 30's in ultra-fine sizes below 0.1 micron.

The first non-black filler having a particle size approaching that of carbon black was calcium silicate, first produced in 1939. Finally, in the early 40's, calcium silicate and calcium carbonate fully comparable to carbon black in particle size were produced.

Hydrated silica with a particle size equal to the finest carbon blacks appeared in the early 50's. This was followed by anhydrous silica of still smaller particle size. Non-black fillers, through the hydrated and anhydrous silicas, have particle sizes as small as any filler available, including carbon blacks. They provide uniquely high tensile strength, tear strength, flex resistance and stiffness. Abrasion resistance approaches, but does not yet equal that of the highest reinforcing fillers. Developments within the last year point the way to overcoming even this disparity between non-black fillers and carbon black.

Together, these inexpensive rub-

CHRONOLOGY OF NON-BLACK PIGMENTS

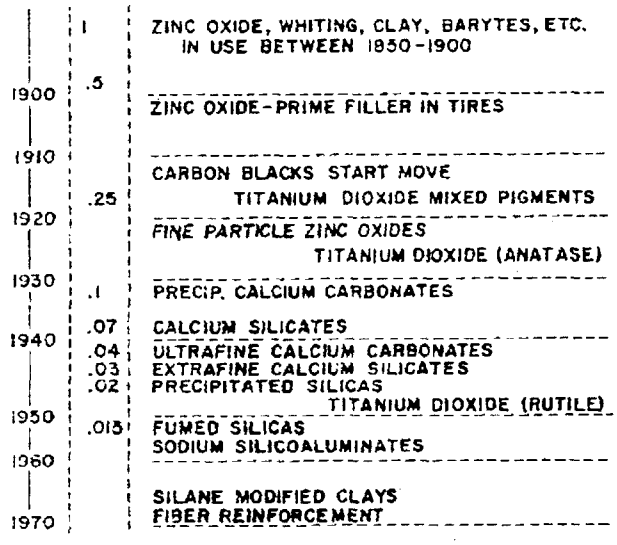

Fig. 1. The first non-black filler having a particle size (center column) approaching that of carbon black was calcium carbonate. Today, hydrated and anhydrous silicas have particle sizes as small as any reinforcer.

Table 1. Composite recipe (in pounds) for rubber industry in 1967.

Natural Rubber	33	100 Lbs. Rubber
Synthetic Rubber	67	
Carbon Blacks	44	44 Lbs. Black
Whitings	(17) Est.	48 Lbs. Non-Black
Kaolin	15	
Zinc Oxide	4.4	
TiO_2 + Barytes	2.3	
Talc	1.2	
Misc. Non-Black Filler	(8.3) Est.	

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MATERIAL CONSUMPTION IN RUBBER INDUSTRY

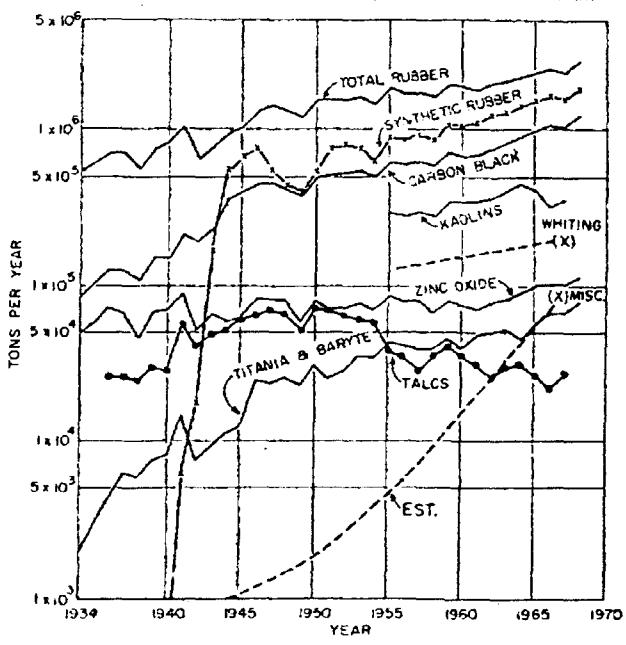

Fig. 2. Total consumption of non-black fillers for rubber is expected to climb to 1,300,000 tons by 1975.

ber fillers account for an estimated 200,000 tons per year, almost as much as carbon blacks (Fig. 2). Talc consumption is decreasing, probably because other fillers are displacing it on a cost/performance basis. The growth of titanium dioxide and barytes is slightly greater than that of rubber, indicating that color is becoming a more important factor in the rubber industry.

The most rapid growth in non-black pigments is occurring, however, in the miscellaneous category. Admittedly this is an estimate, but a reasonable one. Included in this class are precipitated calcium carbonates, calcium silicates, silicoaluminates, hydrated silicas and anhydrous silicas. Figures for most of these products are unavailable, but 200,000 tons per year represents a good estimate.

That non-black fillers, collectively, make up a sizeable portion of the rubber industry can be seen very readily from a composite rubber "masterbatch" of these materials (Table 1). For every 100 pounds of rubber, 67 of which are synthetic, there are 48 pounds of various non-black fillers vs. 44 pounds of carbon black. Of the 48 pounds of non-black pigments, two-thirds of these are whiting and clay. The remaining one-third include 6 or 8 principal materials and an even larger number of very minor components. It is interesting to note that zinc oxide is utilized at levels typical for a vulcanization activator, emphasizing its minor role as a filler. White sidewalls of tires represents its dominant use as a filler.

Today's role of non-black fillers: general classification

The classification of rubber fillers begins with particle size (Fig. 3). On this basis, it is possible to approximately classify non-black fillers according to their reinforcement of rubber. Solid particles larger than about 5 microns act to degrate properties—while most fillers are intended to be smaller, inefficient separation during manufacture may leave a significant fraction of coarse particles in the filler to lower rubber properties.

Those fillers with particles between 1 and 5 microns contribute very little to the strength of rubber. Large volumes can be used without seriously impairing strength; hence, their classification as diluent fillers. Good grades of whiting and soft clays are the dominant products here.

Below about 1 micron, most filler particles begin to reinforce. Hard clays and coarser precipitated calcium carbonates are the principal semi-reinforcing fillers. Zinc oxide and titanium dioxide also fall in the semi-reinforcing range, but are seldom used for this purpose.

Real enhancement of rubber strength is obtained with filler particles below 0.1 microns. Ultrafine calcium carbonates, silicoaluminates, calcium silicates, hydrated silicas and anhydrous silicas provide increasing reinforcement with decreasing particle size. The last two of these are below 0.025 microns in diameter, comparable to ISAF and SAF carbon blacks in size.

The decrease in particle size is, of course, accompanied by an increase in cost. The price of the common fillers range from $0.005-$0.08 per pound. Zinc oxide and titanium dioxide are somewhat higher, while the anhydrous silicas are considerably higher.

Calcium carbonates

Calcium carbonates are available in a range of particle diameters. Those produced from natural forms of calcium carbonate are selected principally on the basis of origin and purity (Table 2). Common types vary in crystal structure and hardness. The softest, and hence the finest, is soft limestone or chalk, commonly termed whiting. These are the most widely used diluent fillers, and generally are the purest and most white, depending on the deposit.

The presence of very coarse particles, chiefly quartz and mica, is the next most important consideration (Fig. 4). Even the best grades of whiting, if they contain a small amount of coarse particles, will not provide the best properties. Tear strength is severely reduced by even a couple percent of residue on a 325-mesh screen. Tensile strength and modulus are noticeably affected, also.

For higher strength and color potential at moderate cost, the finer synthetic calcium carbonates are required (Fig. 5). A rather smooth increase in reinforcement is evident in tensile strength, tear strength, and abrasion resistance as the coarser hard limestones are replaced by the finer soft whitings and, finally, by very fine precipitated calcium carbonate. For optimum dispersion, the ultra fine calcium carbonate is frequently surface coated with oil or fatty acid.

Clays

Rubber grade clays are chiefly kaolins, which occur predominantly in the southeastern United States. Two common grades are recognized by compounders (Fig. 6): soft, coarse-sized clays for producing soft rubber compounds, and small particle-sized hard clays for harder rubber stocks.

Two processing treatments are used to finish the clays. Classification by air, termed air-floated, is the most common. This is an efficient method

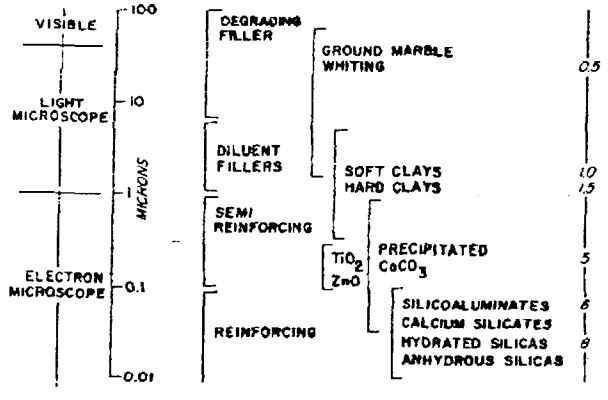

Fig. 3. Classification of rubber fillers is by particle size, which also approximates their reinforcing status.

Table 2. Calcium carbonates produced from natural forms are selected principally on the basis of origin and purity.

1. ORIGIN —	Chalk (Whiting)
	Saccharoidal
	Marble
2. PURITY —	Quartz, Mica
	Calcium Oxide (pH)
	Trace Metals (Cu or Pb)
3. MOISTURE	
4. COLOR	

that removes very large particles, but depends on the deposit for purity, color, etc.

Water-washed clays are generally lighter in color and more uniformly controlled for pH and particle size distribution. Very large particles are readily removed by screening the slurry of clay dispersed in water. Size distribution is controlled by isolating selected portions after settling in large tanks. More efficient separation of coarse and fine fractions is possible by this method.

A convenient though not precise way to characterize kaolins is the "percent less than 2 microns." The extremes in hard and soft clays are obtained by water classification (Fig. 6), while the air-floated clays generally have a broader particle size distribution and are not as clearly different in rubber as are the water washed varieties.

Special treatments of clay are aimed at improving dispersion, increasing whiteness or reducing water absorption. Various organic surface active materials improve dispersion and, hence, rubber properties. Chemical treatment during water washing removes colored impurities such as iron and copper and increases whiteness. Calcining removes bound water between crystal layers and, consequently, reduces water absorption.

Silicas and silicates

The highest reinforcing non-black pigments are the fine particle silicas and silicates. Rubber shoe soles surpassing leather in wear, comfort and flexibility contain one or more of the several pigments available in this class.

Hydrated silica imparts exceptional tear resistance to most rubbers, and is used with carbon black to obtain maximum mileage in tires for mining and logging operations and for road building equipment. These and other

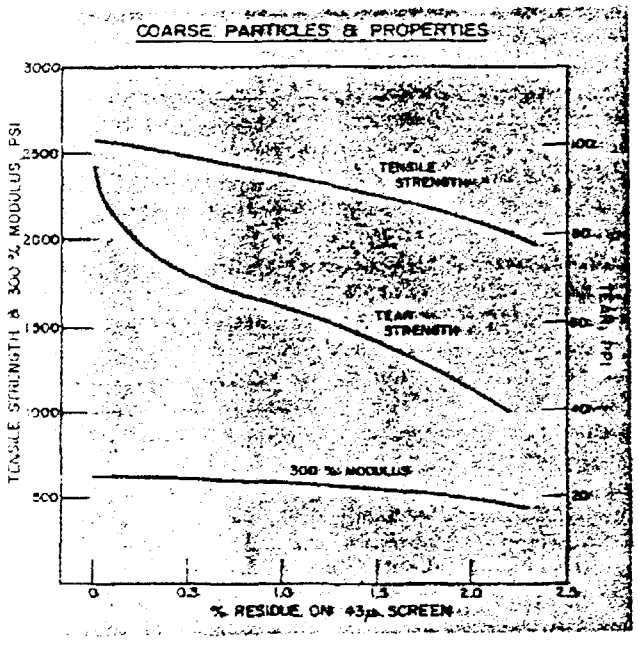

Fig. 4. The presense of coarse particles in calcium carbonate reduces effectiveness in rubber reinforcing.

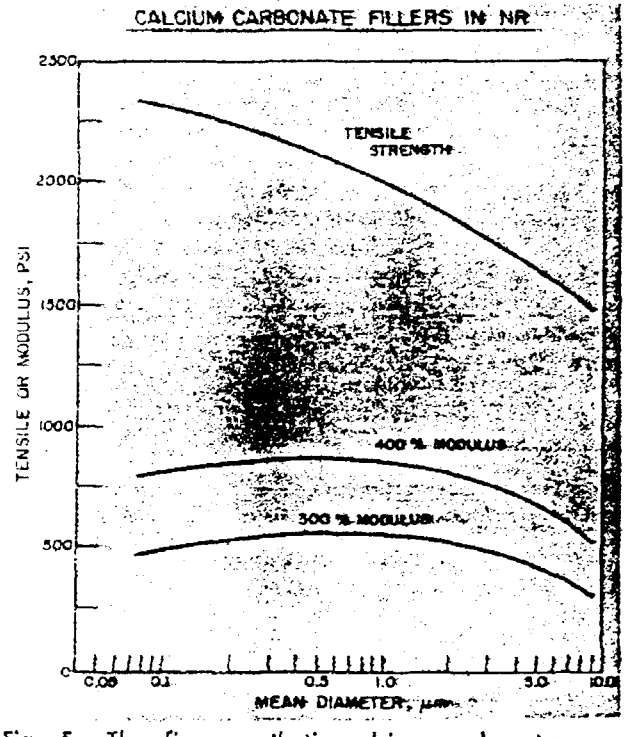

Fig. 5. The finer synthetic calcium carbonates are required where higher strength and color potential at a moderate level of reinforcer cost are called for.

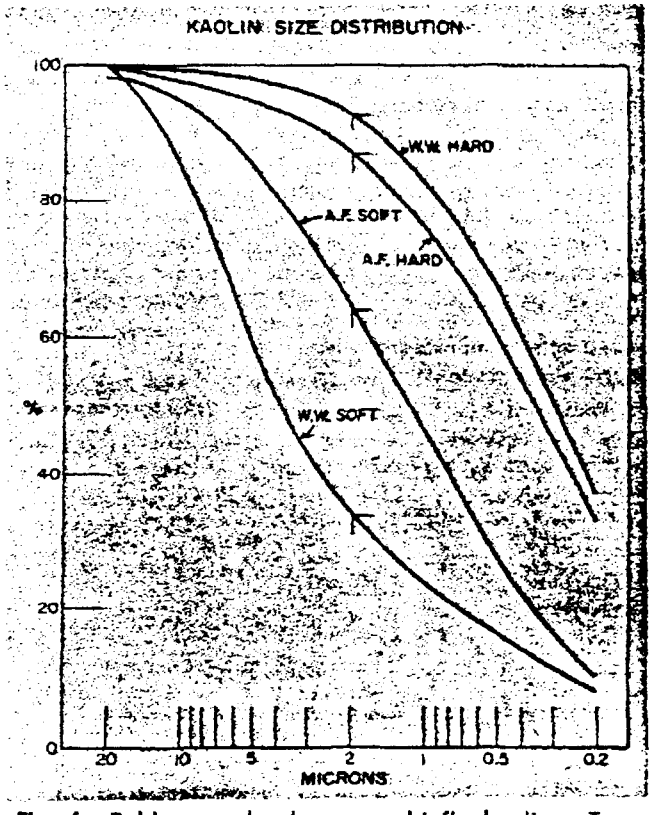

Fig. 6. Rubber grade clays are chiefly kaolins. Two common grades used by compounders include: soft, coarse clays for soft compounds; and hard, small particle-size clays for compounding harder rubbers.

applications have become well established over the past 20 years.

Anhydrous silicas have the smallest particles available in non-black fillers. They also are very pure silica and have very low moisture. Consequently, they are chiefly used in silicone rubber for electrical applications. Demanding requirements for very high temperature reinforcement, low moisture sensitivity and high electrical resistivity justify the high cost of anhydrous silicas and silicone rubber in such applications.

The properties of silicas and silicates available in the U. S. differ, first of all, in chemical composition (Table 3), due to the raw materials and manufacturing method. The first four materials are made in an aqueous system by converting water-soluble silicates into insoluble silica or silicates by use of acids or salts. The products contain 65 to 88% silica and up to 22% of other metal oxides. Under normal conditions they will also have 4-6% of adsorbed water. Not shown is the bound water, which, in each case, amounts to about 5%.

Anhydrous silica is made by an entirely different process. Silicon tetrachloride is oxidized directly to silica by reaction with water and oxygen at elevated temperatures. The resultant product is essentially free of bound water, adsorbed water and metal oxides.

The particle size varies according to the specific product, and is controlled in the manufacturing process. The degree of reinforcement is again determined by particle size (Fig. 3).

Current uses of non-black fillers

The variety of rubber articles utilizing non-black fillers is tremendous, but their principal applications are based on specific attributes which can be grossly generalized as follows: whitings have as their chief utility low cost with a minimum of change in rubber properties; clays and precipitated calcium carbonates impart moderate properties at moderate cost; the hydrated silicas and silicates impart high tensile strength, tear strength and abrasion resistance. All, of course, are suitable for colors other than black, but titanium dioxides are required for white or pastel colors.

Fillers quite often are used in combination to gain the unique properties of each type, and sometimes there is a synergistic increase in properties when two or more fillers or compounding ingredients are used together. An example of this is the use of whiting in combination with hydrated silica (Fig. 7). Tear resistance as a function of silica and whiting levels was obtained from an

Table 3. Typical compositional properties for silicas and silicates available in the United States.

	Calcium Silicate[a]	Sodium Silico-Aluminate[b]	Hydrated Silica		Anhydrous Silica[e]
			Reinf.[c]	Reinf.[d]	
SiO_2, %	65	65	80	88	98
CaO, %	20	..	5	..	..
Al_2O_3, %	..	12	..	..	..
Na_2O, %	..	10	..	..	..
Moisture	5	4	6	5	1
pH	10	10	9.5	7	4
Particle Size, microns	0.03	0.04	0.08	0.02	0.015

[a] Silene EF, PPG Industries, Inc.
[b] Zeolex 23, J. M. Huber Corp.
[c] Silene D, PPG Industries, Inc.
[d] Hi-Sil 233, PPG Industries, Inc.
[e] Cab-O-Sil M-5, Cabot Corp.

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Table 4. Tear strength with Hi-Sil 233.

Natural Rubber (SMR-H-5L)	100			
Zinc Oxide	5			
Stearic Acid	1.5			
Sunolite 240	1.5			
Wingstay 100	1.0			
Thermoflex A	1.0			
Plastogen	5.0			
Hi-Sil 233	45	45	..	15
EPC Black (S-300)	..	..	45	..
HSAF Black (N-285)	..	..	..	30
Sulfur	2.5	2.5	2.7	2.5
Santocure NS	1.4	1.0	1.0	1.0
TMTD	0.5	.5	..	.2
Mercaptosilane	..	1.0	..	..
ML 4 - 212	96	77	57	78
Mooney Scorch, Min./270°F	12	11	17	12
90% ODR Cure, Min./300°F	9	7	17	10
300% Modulus, psi	620	1000	1390	1380
Tensile Strength, psi	3780	3860	4100	3830
Elongation, %	700	660	580	570
Hardness	60	62	60	60
Tear, Die C, ppi	470	620	380	390
Slit Tear, ppi RT	217	187	80	110
170°F	171-296[a]	193-340[a]	130	68-168[a]
Compression Set, % (B)	25	15	29	19

[a] Knotty Tear

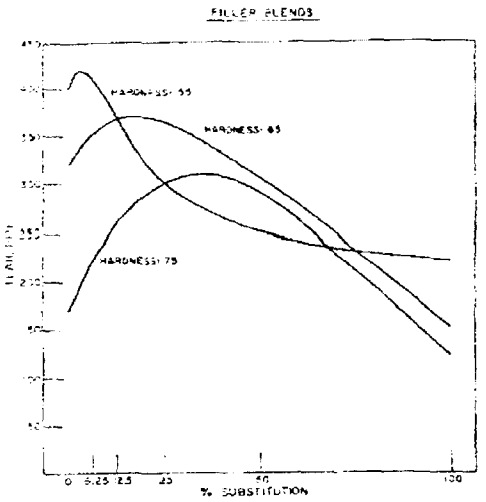

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Fig. 7. Combinations of fillers such as whiting and hydrated silica are often employed to gain some combination of the unique but complementary qualities.

Table 5. Adhesion with the HRH modification of a typical carcass stock for passenger car tires.

	A	D
Natural Rubber	70	70
SBR	30	30
SRF Black	45	30
Hi-Sil 233[3]		15
Zinc Oxide	5	5
Stearic Acid	2	2
Process Oil	4	4
Resorcinol		2.5
MBTS	0.85	0.85
DPG	0.35	0.35
Sulfur	2.4	2.4
Hexamethylenetetramine		1.6
Strip Adhesion, pounds per inch		
Nylon (Greige)	1.5	90+
Rayon (Greige)	3.0	55

Table 6. HRH adhesion to wire.

	Adhesion[c], lbs. A	D
Brass-plated wire[a]:		
Original (@ R. T.)	77	196
Aged[b] (@ R. T.)	64	164
Aged[b] (@ 250°F)	68	150
Bare steel wire:		
Original (@ R. T.)	41	70
Aged[b] (@ R. T.)	35	60
Aged[b] (@ 250°F)	15	23

[a] Wire Cord constructure: 5 x 7 x 3 x 1 (0.0059")
[b] Aged 48 hrs. at 212°F
[c] ASTM D2229-T63, 1-inch pull through

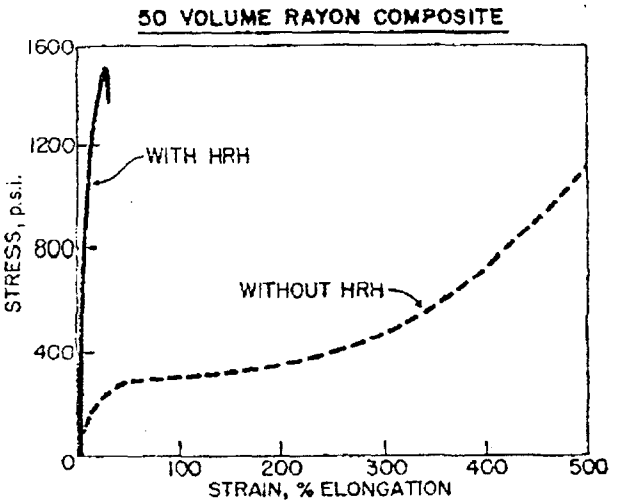


Fig. 8. The HRH system is also used to improve the performance of rubber reinforced with short fibers.

Table 7. Effect of fillers on strip adhesion using resorcinol and hexamethylenetetramine (formulations similar to A and D).

Filler	Strip Adhesion, lbs.[a]
SRF — Black	29
SRF — Hi-Sil 233®	80+
SRF — Silene D®	70
SRF — Silene EF®	80+
SRF — Clay	31

[a] To greige nylon, square woven

Table 8. Wire adhesion with modified HRH system.

Natural Rubber (SMR-H-5L)	100	100
N-330 Black	45	45
Hi-Sil 233	15	15
Stearic Acid	2	2
Antioxidant	3	3
Naphthenic Oil	8	8
Zinc Oxide	5	5
Resorcinol		2.5
Morpholino-sulfenamide	0.8	0.8
Sulfur	3.0	3.0
Cyrez 966[a]		3.0
Cure, Min. 300°F	30	30
300% Modulus, psi	1320	1340
Tensile Strength, psi	2760	2570
Elongation	490	420
Adhesion to Brass-Plated Wire, (3 x 1) + (6 x 1), lb./in.		
Room Temp., Original	69	128
Pulled at 250°F, Original	82	150
Aged 72 hrs./250°F	76	156
Wire covered, %	30-40	90-100

[a] Hexamethoxymethylmelamine, American Cyanamid Co.

experimental design. The resulting equations indicated that somewhat higher tear strength can be obtained by the partial substitution of hydrated silica with whiting. An economic saving is also realized.

In another example of the combined use of fillers (Table 4), the unique tear resistance from silicas and the abrasion resistance from ISAF black were combined in a tread stock for heavy service tires (last column). An all-silica loading is superior to any carbon black, including channel blacks (first column). In an effort to improve wear resistance, a mercaptosilane (Union Carbide's Silane A-189) was added without sacrifice in tear resistance (second column).

New developments in non-black pigments: adhesion

Non-black pigments are not confined to their traditional role of filler. One such exciting field of use is to promote adhesion of rubber to a variety of materials. Those fillers with small particle sizes are more effective. Zinc oxide has been noted for its ability to improve tack and adhesion of rubber.

Hydrated silica improves the adhesion of non-polar rubbers to metal and polyurethanes. In combination with certain resin formers, adhesion to untreated cord and metal is outstanding. In fact, this combination of ingredients—called the HRH system and including Hi-Sil 233 (precipitated, hydrated silica), resorcinol and hexamethylenetetramine—is an effective method of obtaining adhesion to fibers and wire without need for cement or latex dips. As such, it is being used in belts, hose, proofed fabrics, and other fabric reinforced rubber goods. To some degree, the HRH system is also used in tires.

The essential features of this technology are shown in Table 5. While adhesion of the carcass compound to RFL-dipped cord is excellent, its adhesion to greige (or un-dipped) nylon or rayon is very low. However, the adhesion levels for both un-dipped fibers can be enormously improved by using the HRH system of Hi-Sil 233, resorcinol and hexamethylenetetramine.

Actually, when properly compounded, the HRH system provides adhesion to greige cord surpassing that of RFL-dipped cord. Retention of adhesion at high temperatures and after aging is also excellent.

Adhesion values for wire are also greatly improved with this system: by the simple addition of the HRH components to a conventional carcass formulation, adhesion values are approximately doubled (Table 6). The HRH system is particularly effective with brass-plated wire used in tires, belts and hose. Even at high temperatures and after aging, adhesion is still high. While not as high, adhesion to bare steel wire is still respectable.

When using the HRH system, however, it is essential that all ingredients be well dispersed and that premature reaction of hexa and resorcinol be avoided. Crystalline resorcinol can be added in the Banbury at a sufficiently high mix temperature to effect dispersion. Alternatively, it can be added in the form of a rubber masterbatch or as a co-blend with stearic acid. These are readily dispersed in the Banbury or on the mill.

Hexamethylenetetramine must be in a dispersible form and must be added at temperatures below 250°F. Several forms are available, including Hexa Flo Powder, a rubber masterbatch and various oil pastes.

Not all fillers function in the HRH system (Table 7). Only the fine particle silicas and silicates promote adhesion. Apparently, the high energy surface and high surface area associated with small particle size are required.

Further, while hexamethylenetetramine is an active component, objections to its use can be overcome by using alternate materials. Two such materials are available: hexamethoxymethyl melamine (Cyrez 966) and a similar material, Cohedur A. For example, Cyrez 966 readily gives adhesion values comparable to those previously shown for nylon and brass-plated wire; again, effectiveness at high temperature and after aging is demonstrated (Table 8).

Fiber reinforcement

Another function of the HRH system is to improve the performance of rubber reinforced with short fibers, another class of non-black fillers (Fig. 8.) Chopped rayon, when added to rubber compounds, provides exceptional stiffness. However, poor adhesion in conventional compounds causes loss of stiffness at moderate extensions. The HRH modification overcomes this fault and provides exceptional strength and flexibility at reduced extensibility.

In one series of tests, three short fibers at 12 volume percent loadings

Table 9. Dynamic properties with fiber reinforcement.

Natural Rubber	100
Hi-Sil 233	12
Filler	12 Vol. % Fiber, or 27 Vol. % FEF Black
Resorcinol	2.5
Zinc Oxide	5
Hexa Flo Powder	1.6
MBTS	0.7
DPG	0.3
Sulfur	2.5

	Rayon	Fiber Glass	Calidria HPP	FEF Black
100% Modulus, psi	1450	1650	2080	460
Tensile	1840	1650	2510	3560
Elongation, %	150	110	120	430
Yerzley				
Dynamic Modulus, psi	1506	1444	2819	1381
Resilience, %	82	88	71	74
Goodrich Flexometer (212° F, 22.5%, 24.5 lb.)				
Heat Build-Up, °F	43	25	61	83
Set, %	9.3	4.7	13.2	16.9

were compared with FEF black at a 25 volume percent loading. The compounds with fibers contained the ingredients of the HRH system. Chopped rayon and fiber glass were typical of undipped tire cord material. Calidria HPP is an extremely fine asbestos fiber with a diameter of only 0.02 microns.

The effective stiffening of the rubber by the fibers was much higher than that of the carbon black. Fiber glass and Calidria HPP had the highest efficiency, perhaps due to a much stiffer fiber.

The high modulus contributed by the short fibers was obtained with considerably less loss of resilience than with conventional fillers. Some of the dynamic properties of these compounds are shown in Table 9. This shows that fiber reinforcement can provide higher resilience and lower heat build-up at a dynamic modulus equivalent to conventional fillers. It is also true that much higher dynamic modulus can be obtained with fiber reinforcement without sacrificing resilience or heat build-up.

The combination of adhesion obtained with the HRH system and the reinforcement produced by short fibers provides a new dimension in engineering with rubber. The increased dynamic modulus/resilience ratio provides greater load support for resilient mounts, rubber bushings and many other applications.

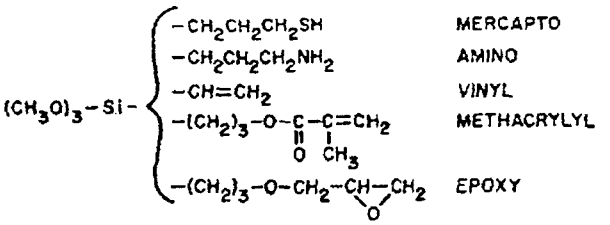
Designed surface activity

The chemical nature of most nonblack pigments suggests that strong bonding with an elastomer is improbable; and in some cases, noncompatability of the filler with the rubber has led to poor dispersion. However, a number of products have been surface modified to improve their performance in rubber. Zinc oxides, precipitated calcium carbonates and clays have been coated with surface active materials to improve dispersion and make the fillers more effective. Recently, clays have been modified with chemically reactive silanes to substantially improve the properties they impart to rubber.

It is, in fact, possible to tailor the reactivity of the filler surface to provide chemical bonding with the rubber. Organofunctional silanes (Table 10) are effective materials for this purpose. Methoxysilyl (left side) reacts readily with fillers containing silanol groups—e.g., clays, silicas and silicates. The functional group on the right is chosen to react specifically with the rubber system. For most sulfur cured polymers the mercaptosilane is effective (the example at the bottom indicates the nature of the

Table 10.

ORGANO FUNCTIONAL SILANES



TYPICAL FILLER–RUBBER BONDING:

FILLER Si–O–Si–$CH_2CH_2CH_2$–S–CH_2– RUBBER

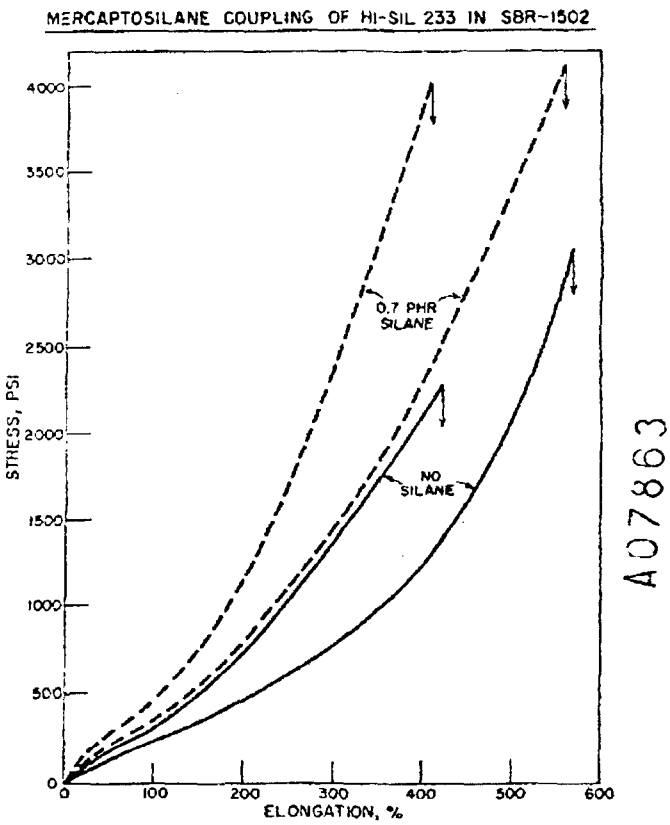


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Fig. 9. Mercaptosilane significantly improves modulus and tensile strength of silica-filled SBRs. Two cure states show better crosslinking with coupling.

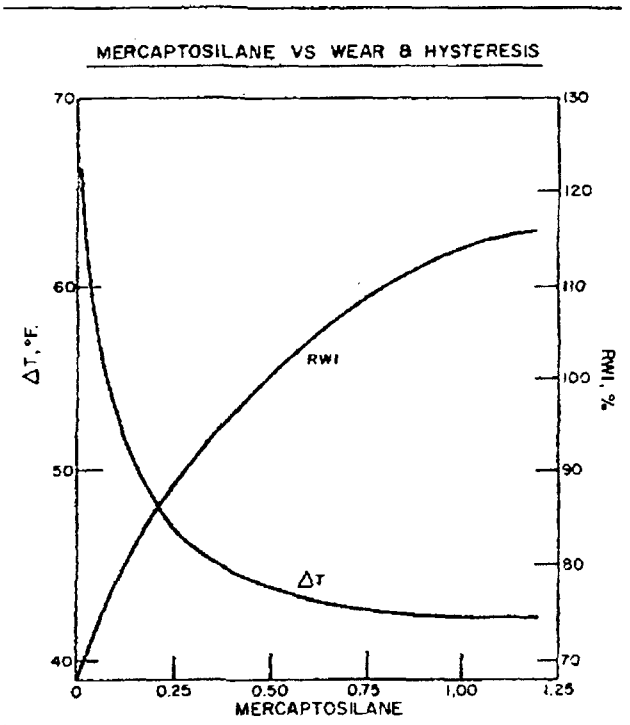

Fig. 10. Even small quantities of mercaptosilane—less than 0.5 phr or 1 per cent on the silica—reduces heat build-up by 25°F; increases tread wear by 40 per cent.

filler-rubber attachments).

Thus, it is possible to introduce one or more rubber-functional groups on the surface of the filler. For polyurethane systems the amino- and epoxy- silanes are effective; for peroxide cured rubbers the vinyl and methocrylyl are effective.

The effect of mercaptosilane on a silica-filled SBR is shown in Figure 9. The SBR vulcanizate containing 60 phr of Hi-Sil 233 and 0.7 phr of mercaptosilane shows a significantly greater stress at all elongations, leading to higher modulus and tensile strength, than an identical SBR vulcanizate containing 60 phr of Hi-Sil 233 but no silane.

Two cure states for each are shown to emphasize that an effective increase in crosslinking occurs with the coupling reaction. This automatically gives higher modulus, but coupling produces greater strength.

This coupling technology has shown tremendous improvements in rubber properties containing hydrated silica or clay. In clay-filled EPDM, mercaptosilane increases modulus and tensile strength significantly. At the same time, elongation and heat build-up are reduced.

Similar changes are seen to occur in clay-filled polychloroprene. Here, the reduction in elongation is quite large, indicating a substantial increase in effective cure state with mercaptosilane. This alone accounts for a sizeable increase in modulus. Even so, the retention of tensile strength at the high state of cure indicates significant coupling activity.

In polyurethane rubber, the aminosilane is an effective coupling agent. The very large increase in tensile strength indicates coupling between the clay and the rubber chains.

To obtain maximum abrasion resistance, a combination of small particle size and high filler-rubber interaction seems essential. Extensive evaluations have been carried out in silica-filled rubbers. A few of these will be reported.

In SBR, mercaptosilane improves the reinforcement with Hi-Sil 233 (Table 11). A typical Hi-Sil-filled SBR was compared with and without mercaptosilane and also with the tread black compound. Mercaptosilane increases modulus and tensile to values comparable to those of the black compound. At the same time, heat build-up is reduced to practical

Table 11. *Effect of mercaptosilane coupling on a Hi-Sil-filled SBR compound.*

SBR 1502	100	100	100
Hi-Sil 233	60	60	
N-285 Black			60
Process Oil	10	10	10
Zinc Oxide	4	4	4
Stearic Acid			2
PBNA	1	1	1
Flexamine	1	1	1
MBTS	1.5	1.5	0.8
DOTG	1.5	1.5	0.3
Sulfur	2.75	2.75	1.85
Carbowax 4000	1.5		
Mercaptosilane		1.5	
ML 4 - 212	100	77	76
300% Modulus, psi	720	1980	2210
Tensile	2690	3770	3510
Elongation, %	580	460	460
Hardness	71	67	74
Goodrich Flexometer ΔT, °F	85 (BO)	49	73
Compression Set, % (B)	25	12	20
Pico Abrasion Index, %	81	131	170
Road Wear Index	79	114	110

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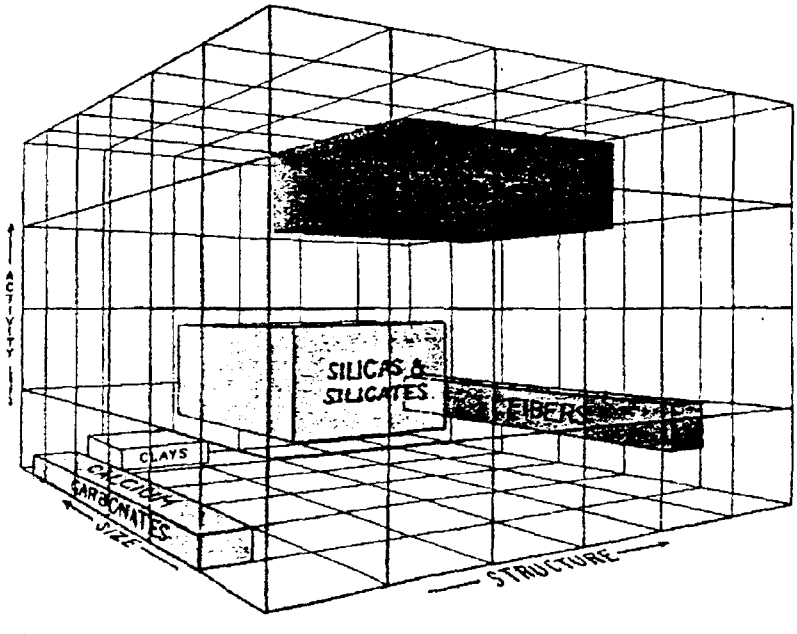

Fig. 11. The broad spectrum of particle size and structure of non-black fillers already provides a wide variety of properties; but, with the coming of tailored surface activity of these fillers, the possibilities for improved modified rubbers could become enormously greater in the future.

levels. The most significant change was in tread wear. Mercaptosilane improved the Road Wear Index of the Hi-Sil tread from the 80% level to the 110% level or equal to the black tread.

The effect of mercaptosilane on heat build-up and tread wear is remarkable (Fig. 10). Even very small quantities, less than 0.5 phr or 1% on the silica, reduces heat build-up by 25°F and increases tread wear by 40%. Maximum benefit to tread wear occurs at about 2% on the silica. This demonstrates the flexibility of this technique in that properties can be adjusted to meet requirements.

Similar property improvement is obtained with mercaptosilane in a modern passenger tread. Using a blend of oil extended SBR and polybutadiene, tread wear equivalent to the black control was realized. Laboratory properties were unable to predict this increase in abrasion resistance. This emphasizes the care that must be exercised in comparing black and non-black pigments on the basis of laboratory properties alone.

In a nitrile rubber (Table 12), mercaptosilane is similarly effective. Only 1.2 phr of the silane enhances modulus nearly threefold, while decreasing compression set to acceptable levels. A decrease in viscosity, a benefit frequently obtained with the silane, is observed in this data. Further, the mercaptosilane has no effect on aging in this sulfurless cure. Abrasion resistance is significantly increased, evidence that reinforcement is improved through coupling.

Many other studies have been conducted in natural rubber, EPDM, chloroprene rubber and epichlorohydrin rubber. All respond to the coupling activity of mercaptosilane. Much improved modulus, tensile and dynamic properties are obtained in all polymers.

The cost of the improvement obtained with silane coupling may be uneconomical for many applications. However, the special requirements of some rubber products can only be achieved in this manner. These include nitrile, EPDM and epichlorohydrin compounds which need high resilience, low set, gas permeability, and in some cases color that can only be obtained through a silica-silane combination.

Future of non-black pigments

What of the future of non-black pigments? There will, of course, be continued growth in the existing products. There will also be new varieties of some. For example, there is a demand for a non-black pigment with better resilience and modulus and with more normal viscosity and cure behavior. Such a product will be forthcoming in a few months.

Look for new innovations in the application of fibrous fillers. With increased bonding, the full utilization of fiber character can be obtained.

Tailoring of surface activity of non-black fillers will become commonplace. The possibilities are enormous. Some examples have been shown in this presentation, but it is possible to speculate even further.

Heretofore, filler particle size and structure have been varied at will, but surface activity has either been low or high (Fig. 11). Beneficial properties are obtained at both ends of the activity spectrum. For example, high tear strength is apparently associated with low activity, while high abrasion resistance requires high activity. We have seen that it is possible to obtain both in a single pigment by adjusting surface activity.

Placing of rubber pigments in this cube (Fig. 11) shows that a wide variety of properties is already available. Examples of low and high surface, structure and activity are present in a number of materials. None possess the potential for all variations. Several which have wide flexibility in particle size and structure are amenable to changes in surface activity. The silicas, for example, already exist in a range of particle sizes and structures, and their activity can readily be altered by using silanes. Other possibilities also exist.

The future of non-black fillers is exceptionally bright. Perhaps a more universal filler will eventually exist which will have the flexibility of variable size, structure and activity by the judicious choice of special compounding additives. At present, this pigment may well be a non-black one. □

AUTHOR Melvin P. Wagner of PPG Industries predicts an exceptionally bright future for non-black fillers.

Table 12. Effect of coupling agents: NBR - *Sulfurless Cure.*

Medium High Nitrile Rubber	100.0			
Zinc Oxide	5.0			
Stearic Acid	2.0			
Lubricant	1.0			
DOP	10.0			
Antioxidant	1.0			
Hi-Sil 233	70.0			
TMTD	3.0			
Sulfur	0.2			
A-189			1.2	
ML-4 212	106		82	
Stress-Strain at 10'/300	Original	Aged[a]	Original	Aged[a]
300% Modulus, psi	820	..	2010	..
Tensile, psi	3060	3080	3640	3570
Elongation, %	570	560	440	370
Hardness	78	84	78	84
Compression Set, % (B)	35		22	
NBS Abrasion Index, %	86		234	

[a] 70 Hrs. @ 212°F

Rubber World
NOVEMBER, 1971

Compounding with fibers for high performance elastomer compounds

Studies indicate that while elastomeric composites loaded with short inorganic 'fiberettes' can be easily dispersed directly in a Banbury or on a mill, it proves more advantageous with organic fibers—particularly with high loadings—to first prepare a stiff fiber-rubber masterbatch, and then incorporate this stiff masterbatch into the main compound.

by George C. Derringer
PPG Industries, Inc.
Barberton, Ohio

Discontinuous fibers, because of their large length-to-diameter ratios, are potentially very effective fillers for modulus reinforcement of elastomers. This is illustrated in the equation by Guth[1]:

$$G = G_0 (1 + 0.67 fc + 1.62 f^2c^2)$$

where: c = volume concentration of filler
f = length-to-diameter ratio of filler particle
G = modulus of filled compound
G_0 = modulus of unfilled rubber

At a given fiber concentration, modulus increases with the square of the length-to-diameter ratio. Thus, since the length-to-diameter ratios of the fibers employed in this study are in the vicinity of 10-50, the modulus of the resulting composites can be expected to be 2-3 orders of magnitude greater than obtainable with reinforcing blacks. This equation is only valid, however, when good adhesion exists between fibers and elastomeric matrix. Unfortunately, without special additives, adhesion between most fibers and elastomers is typically very poor.

HRH system

A tricomponent system consisting of hexamethylenetetramine, resorcinol and fine particle hydrated silica (i.e., HRH) has been found[2] to bring about extremely good adhesion between most types of elastomers and most common woven fabrics. Good adhesion was also found to result when the HRH system was added to many discontinuous fiber-elastomer composites[3]. This is illustrated in Figure 1 which shows stress strain curves for an SRF filled NR/SBR compound containing chopped, uncoated fiber glass with and without HRH. The formulations are given in Table I.

Without HRH the composite exhibited high modulus up to approximately 30% elongation. Beyond this strain (stress) level, however, the fiber-matrix adhesion apparently failed, resulting in poor, high strain modulus. The composite with HRH, on the other hand, exhibited a nearly linear stress strain curve and modulus

PHASE MICROSCOPE had to be used to get details of microtomed composites such as the above fiber glass *in rubber composite (magnification,* 400X). Microscope provided sharper contrasts between matrices and fibers with similar refractive indices.

[1] E. Guth, R. Simha and O. Gold, Kallold Zeit., 1936, 74, 266, Thesis, Vienna, 1937.

[2] Degussa Technische Berichte, "Adhesion of Rubber Compounds on Textiles and Metals" (1957).

[3] Derringer, G. C., Advances in Chemistry Series, No. 99, 1971

Table I. Fiber glass—NR/SBR composite with and without HRH.

	Parts by Weight	
	(without HRH)	(with HRH)
Natural Rubber	70	70
SBR 1712	30	30
SRF	30	30
Hydrated Silica[a]		20
Zinc Oxide	5	5
Stearic Acid	2	2
Napthenic Oil	4	4
Fiber Glass[b]	150	150
Resorcinol[c]		2.5
Hexamethylenetetramine[d]*		1.6
Benzothiazyl Disulfide*	0.85	0.85
Diphenylguanidine*	0.35	0.35
Sulfur*	2.4	2.4

[a] Hi-Sil 233, PPG Industries, Inc.
[b] L49M, chopped to 1-inch lengths, PPG Industries.
[c] Technical grade.
[d] Hexa Flo Powder, Heyden Chemical Div., Tenneco, Inc.
* Added on mill.

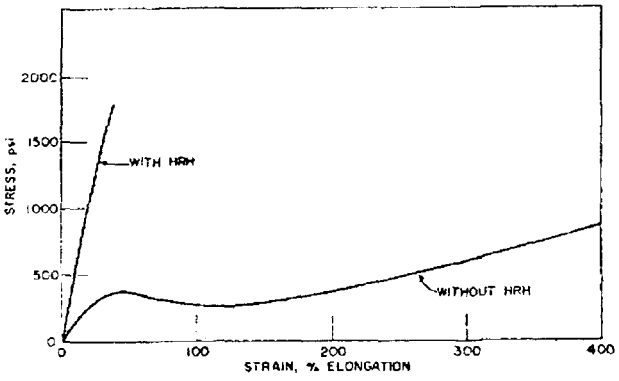

Fig. 1. HRH effect on fiber glass —NB/SBR composite.

Table II. Standard polychloroprene formulation containing HRH.

Polychloroprene[a]	100
N-phenyl-alpha-napthylamine	2
Magnesium Oxide	4
Hydrated Silica	25
Naphthenic Oil	15
Resorcinol	1.7
Stearic Acid	2.5
Diorthotolylguanidine*	0.5
Sulfur*	1.0
Hexamethylenetetramine*	1.6

[a] Neoprene W, E. I. duPont.
* Added on mill.

levels higher than can be obtained with conventional reinforcing pigments.

Variation with fiber loading

Variation of stress strain properties with fiber loading is illustrated in Figures 2 and 3 for fiber glass in polychloroprene formulation is given in Table II. For modulus, tensile and elongation the following empirical equations have been found adequate for most of the fiber and elastomer types investigated[3],

Young's Modulus

$$G = G_0 - 1 + \exp(aV^b)$$

Tensile

$$T = T_0 + cV - dV^{1/2}$$

Elongation

$$E = E_\infty + (E_0 - E_\infty) \exp(-fV^g)$$

where:

G = Young's modulus of composite, psi
G_0 = Young's modulus of matrix compound, psi
T = Tensile strength of composite, psi

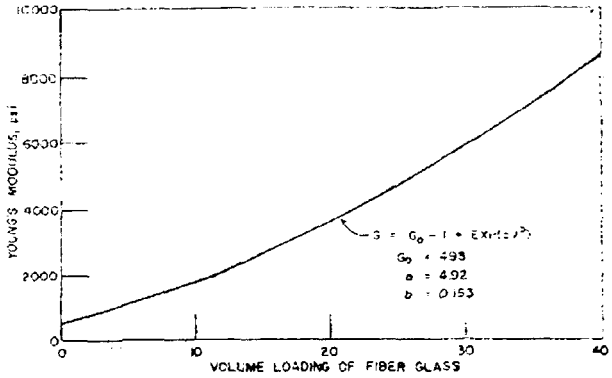

Fig. 2. Variations of Young's Modulus with fiber glass loading in a polychloroprene compound containing HRH.

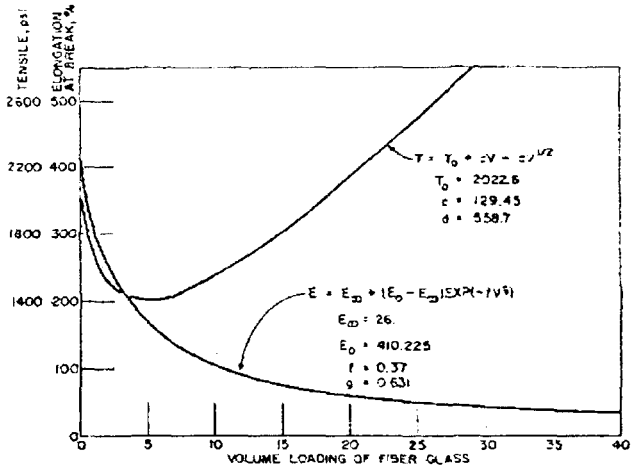

Fig. 3. Tensile and elongation at break; fiber glass loading in a polychloroprene compound containing HRH.

T_0 = Tensile strength of matrix compound, psi
E = Elongation at break of composite, %
E_∞ = Limiting elongation of highly loaded compound
E_0 = Elongation at break of matrix compound, %
a, b, c, d, f and g are empirical parameters
V = volume loading of fiber, cm^3 per 100 g rubber

The modulus curve (Fig. 2) could also be represented by a quadratic function to conform to Guth's model, but the empirical exponential model has been found more flexible and capable of representing all of the fiber composites studied to date.

In Figure 3 it is seen that small fiber loadings have a very large effect on both tensile and elongation. For tensile strength, the initial sharp loss is gradually recovered as the fiber loading is increased. The matrix tensile strength is regained at approximately four times the loading giving minimum tensile, by virtue of the proposed equation. Elongation at break

Table III. Fibers vs. FEF in natural rubber.

Formulations (parts by weight)									
Natural Rubber	100								
Hydrated Silica	12								
Rayon Fiber[a]	9	18							
Fiber Glass			15	30					
Ultrafine Asbestos[b]					15	30			
FEF							35	50	65
XR124R[c]*	4.2								
Zinc Oxide*	5								
Hexamethylenetetramine*	1.6								
Benzothiazyl Disulfide	0.7								
Diphenylguanidine*	0.3								
Sulfur*	2.5								
ODR Rheometer Properties at 300°F									
Minimum Torque, in.-lb.	3.8	2.6	4.0	5.5	5.0	5.9	6.4	9.5	11.3
Maximum Torque, in.-lb.	67.4	78.4	64.4	74.3	79.2	103.0	62.0	67.0	67.9
95% Cure Time, minutes	13.5	14.5	13.5	13.0	15.0	16.5	13.0	14.0	16.5
Stress Strain Properties									
Cure at 300°F, minutes	30	30	30	30	30	30	15	15	15
Young's Modulus, psi	760	1330	840	1960	1400	3376	295	389	486
20% Modulus, psi	150	255	150	360	300	615	70	90	100
100% Modulus, psi	795	1290	885	1680	1140	1890	280	430	565
Tensile, psi	1680	1710	1920	1800	2340	2550	3850	3120	2840
Ultimate Elongation, %	350	195	310	120	295	175	500	420	320
Hardness, Shore A	63	68	57	67	67	82	53	63	67
Compression Modulus at Zero Strain, psi	732		596		1138		596	759	894
Yerzley Oscillograph									
Resilience, %	88	82	91	88	81	72		74	
Dynamic Modulus, psi	1107	1506	995	1444	1709	2819		1381	
Static Modulus	880	1180	760	1140	1010	1670		850	
Goodrich Flexometer (212°F - 163 psi - 17.5%)									
Static Compression, %	19.5	15.6	20.5	16.7	15.1	9.0	20.3	17.2	15.9
Dynamic Compression, %	7.9	3.5	8.7	- 5.1	3.5		8.1	5.4	5.2
Dynamic Drift, %	3.5	8.7	3.6	2.8	14.2		17.2	35.9	33.1
Permanent Set, %	6.5	9.3	6.2	4.7	9.1	13.2	16.0	33.0	29.8
Heat Build-Up, F°	27	43	23	25	39	61	71	120	111
Goodyear Resilience, %	85		84		78		76	70	66

[a] 60 cuts per inch. Microfibers Inc.

[b] Coledrea HPP, Union Carbide.

[c] 60/40 Resorcinol/Stearic Acid Masterbatch, Harwick Standard Chemical Co.

* Added on mill.

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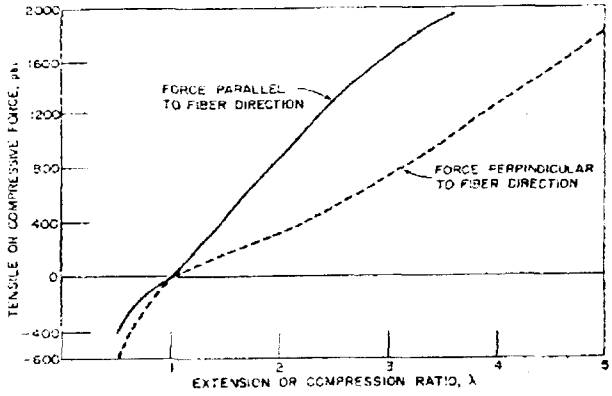

Fig. 4. *Effect of applied force relative to fiber glass orientation on extension, compressive force.*

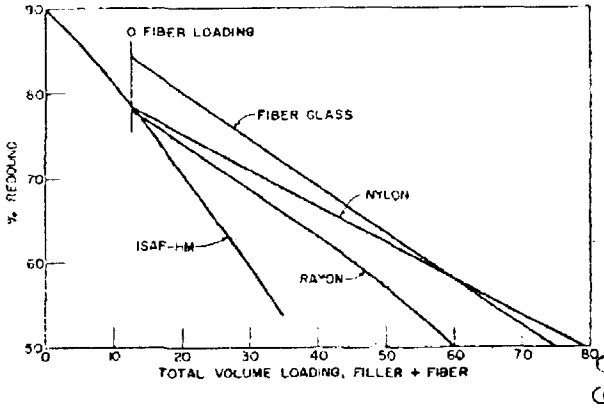

Fig. 5. Effect on Goodyear Rebound; fiber/ISAF-HM.

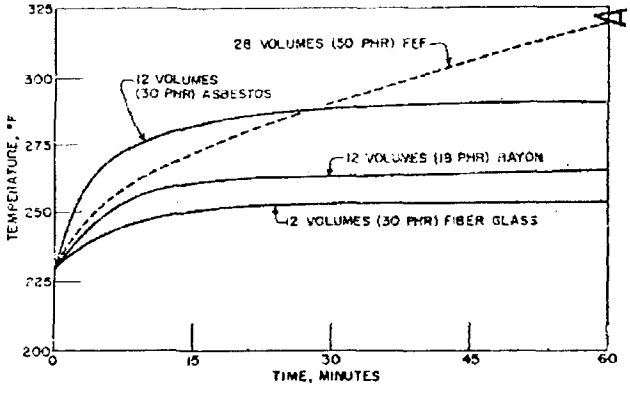

Fig. 6. Effect of fibers and FEF on heat buildup.

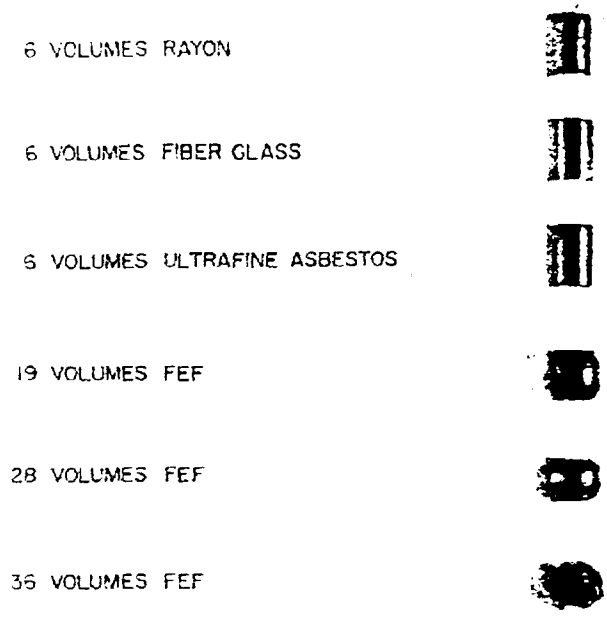

Fig. 7. Comparison of the effects of fibers and FEF on Goodrich Flexometer permanent set results.

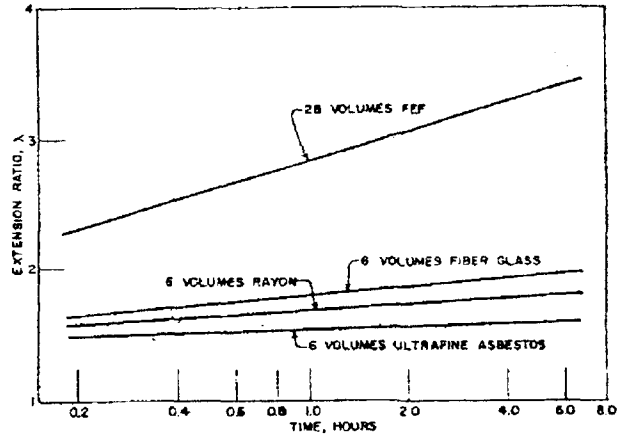

Fig. 8. Comparison of effect of fibers, FEF on creep.

Table IV. Creep behavior of composites vs. FEF filled vulcanizate.

Loading	Increase in Extension per Decade of Time, %
6 Volumes of Rayon	11.0
6 Volumes of Fiber Glass	21.0
6 Volumes of Ultrafine Asbestos	5.0
28 Volumes of FEF	37.5

drops continuously but most rapidly at the lower loadings.

For most of the various types of composites studied, elongation leveled out at 20-50%. Because the rapid loss of elongation with increased fiber loading is found only when good fiber-matrix adhesion is obtained, ultimate elongation is a good index of fiber-matrix adhesion, especially at higher fiber loadings.

NR-HRH composites at low fiber loadings

The remainder of this exposition deals with natural rubber composites containing relatively low volume loadings of fiber glass, rayon, and ultrafine asbestos (Table III). The hexamethylenetetramine was added on the mill to prevent premature reaction with the resorcinol. In all extension tests the fiber was oriented parallel to the direction of applied force. In all compression tests the fiber was oriented perpendicular to the direction of applied force.

Orientation

All rubber compounds demonstrate what is known as a grain effect, or anisotropy. That is, physical properties are dependent upon the direction

of applied stress relative to the grain direction.

The so-called grain is a result of the milling operation, which tends to cause molecular orientation in the milling direction. When the reinforcing material has a length-to-diameter ratio greater than 1 we might expect it to also become oriented during milling. This is actually what happens with fiber reinforcement.

Figure 4 illustrates stress strain curves for a 6-volume (15 phr) loading of fiber glass with HRH in the standard natural rubber formulation shown in Table III. Curves are shown for both extension ($\lambda > 1$) and compression ($\lambda > 1$) with the force applied both parallel and perpendicular to the fiber orientation direction. Lambda, λ, is the extension ratio if λ is > 1 or the compression ratio if λ is < 1. In any case, λ = deformed dimension original dimension.

It is quite interesting that in extension, greatest stress results from a parallel application of force, whereas in compression it results from a perpendicular force application. The compression sample was a cylinder 1 inch in length by $\frac{3}{8}$ inch in diameter. Upon compression the deformation was perpendicular to the direction of applied force rather than parallel, which is the case for extension.

In short, greatest reinforcement is thus obtained when the fiber orientation direction is parallel to the direction of deformation of the test piece. The same general behavior is obtained with high structured blacks such as FEF; however, the magnitude of the effect is much smaller.

For the fiber glass composite, no extra milling was given to the compound so that it was far from completely orientated. If complete orientation could, in fact, be accomplished the two curves in Figure 4 would be considerably more separated.

Higher fiber loadings also increase the degree of anisotropy. The property of anisotropy, previously barely obtainable via conventional compounding, can be very useful in the design of rubber articles.

Modulus and resilience

By far the most unique property of HRH-fiber composites is their extremely high extension modulus. Modulus values can be obtained which are completely out of reach with any type of carbon black presently available. For example, the 20% modulus values in Table III which range as high as 615 psi cannot be matched by an equivalent loading of any existing carbon black. At high fiber loadings (20-70 volumes), Young's modulus values in the 20,000-40,000 psi range have been obtained. This is two orders of magnitude higher than can be obtained with any carbon black.

Perhaps as important as the high modulus is the relatively high resilience which is simultaneously obtained. This applies to both static and dynamic modulus. For example, in Table III, 50 phr (28 vol.) of FEF gave a Young's modulus of 389 psi, Yerzeley static compression modulus of 850 psi, Yerzeley dynamic compression modulus of 1381 psi and a Yerzeley resilience of 74%. The corresponding values for the 30 phr (12 volume) fiber glass composite were 1960 psi, 1140 psi, 1444 psi, and 88%, respectively. Thus at a considerably lower loading, the fiber glass resulted in significantly higher modulus levels, especially in extension, in addition to considerably higher resilience.

The effect of fiber loading on Goodyear resilience is compared to that of ISAF-HM black in Figure 5. The formulation is the same as that of Table III with the exception that 25 phr of hydrated silica was employed instead of 12. Thus the fiber curves begin at a volume loading of 10. It is the slopes of these lines that we are interested in and the fiber glass slope is 0.55 percent per volume vs. 1 percent per volume for the black. In other words, one part by volume of ISAF-HM reduced the resilience about twice as much as an equal amount of fiber glass.

Heat buildup and permanent set

Along with higher resilience, HRH fiber composites exhibited considerably lower heat buildup and permanent set than reinforcing carbon blacks. A comparison of the 9 phr rayon composite with the 50 phr FEF loading illustrates this difference quite well. The two compounds exhibited roughly equal hardness and static compression modulus while the composite had slightly lower dynamic compression modulus. The heat buildup and permanent set of the composite, however, were 27°F and 6.5%, respectively, compared to 120°F and 33% for the FEF.

Figure 6, which shows heat buildup as a function of time, gives a very good comparison of the behavior of the composites vs. FEF black. Whereas the composites reached equilibrium heat buildup at 20 minutes, the FEF vulcanizate exhibited a continual increase until the sample blew out.

Figure 7 is a photograph of the test specimens after 60 minutes of testing. The difference in permanent set is quite striking. Whereas the composites exhibited only very slight dimensional changes, the black compounds were extremely deformed, with the high loading showing a blow out.

Creep

To study creep behavior, the 6 volume loading composites and 28 volume FEF comparison were subjected to a load of 300 psi at 212°F and elongation measured as a function of time. The linear extension ratio vs. log time (hours) plot is given in Figure 8. As can be seen, the composites exhibited considerably lower creep than the FEF in spite of the considerably lower loadings. The values of fractional increase in extension ratio per decade of time are given in Table IV.

Stress softening

Early during the course of work with HRH fiber composites, it was observed that the composites exhibited a rather high degree of stress softening. To determine the importance of this, the 6 volume composites and all three loadings of FEF were stretched repeatedly to 100% elongation. The results are shown in Figure 9. Each curve was fitted to the following equation:

$$G = G_\infty + S \exp[-a(N-1)^b]$$

where:

- G = 100% modulus at any given stretch
- G_∞ = limiting modulus, i.e. 100% modulus after an infinite number of stretches
- S = amount of softening
- N = number of stretches
- a, b = fitted constants

The equation parameters are summarized in Table V. A plot of 100% modulus on the first stretch (i.e., $M_\infty + S$) vs. M_∞ is shown in Figure 10. The slope of the resulting least square line was 0.499. In other words, all vulcanizates (fiber or FEF filled) ultimately lost 50% of their

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Table V. Parameters for softening equation.

$$G = G_\infty + S \exp[-a(N-1^b)]$$

Loading	M	S	a	b
6 Volumes Rayon	380.575	409.365	0.682	0.404
6 Volumes Fiber Glass	351.75	498.258	0.658	0.403
6 Volumes Ultrafine Asbestos	606.82	593.21	0.906	0.447
19 Volumes FEF	176.10	90.90	0.448	0.319
28 Volumes FEF	268.75	134.29	0.833	0.658
36 Volumes FEF	324.11	235.92	0.980	0.489

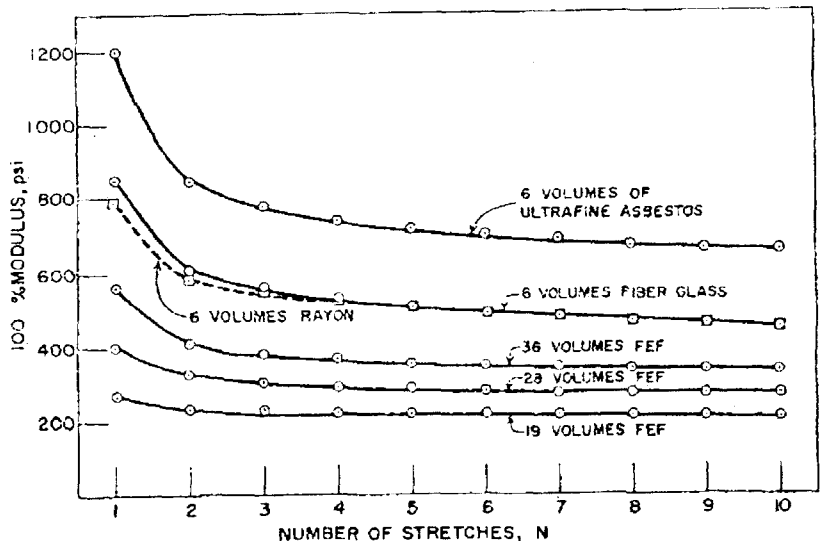

Fig. 9. A comparison of the effect of fibers and FEF on stress softening.

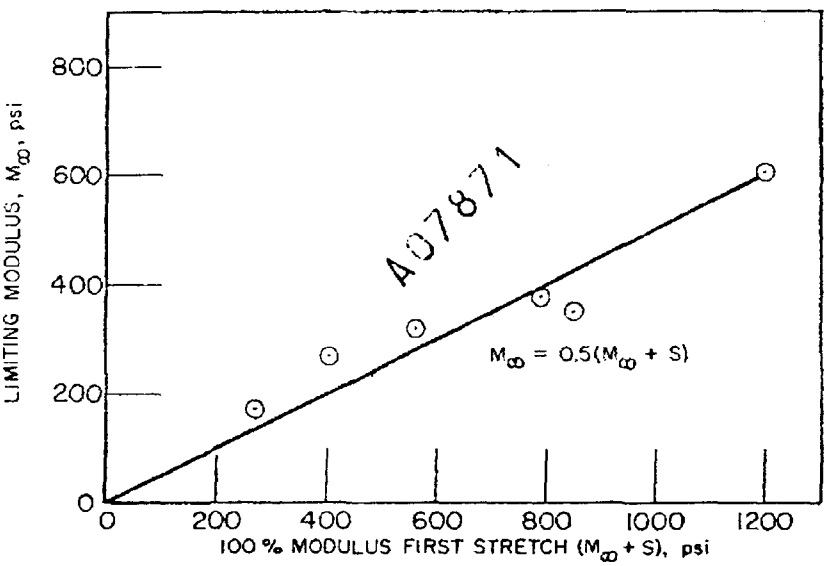

Fig. 10. Initial and limiting modulus; composites and FEF filled vulcanizates.

original modulus so that comparison of modulus on the first stretch is valid.

Processing

Of all the fiber types evaluated, fiber glass is by far the easiest to disperse. It can either be added in the Banbury or on the mill during the final stage of mixing. The latter results in longer fiber lengths because fiber breakage is minimized. Ultrafine asbestos is not as easy to disperse but disperses well when added in the Banbury early in the mix cycle.

Organic fibers such as rayon, nylon, and orlon are quite difficult to disperse, especially at high loadings. For best results, a stiff masterbatch of fiber and rubber, usually at equal parts by weight, is first prepared in the Banbury. This masterbatch is then added in the Banbury to the final compound.

For the HRH system to be effective, resorcinol should be added in the Banbury and the hexamethylenetetramine in the second stage of mix at temperatures lower than 150°F. This prevents premature reactions of resorcinol and hexamethylenetetramine. It is further recommended that the hydrated silica constitute at least 1/3 of the total pigment loading.

Fiber and elastomer types

To date, rayon, orlon, fiber glass, asbestos, and nylon have been found to be effective in HRH composites with natural rubber, NBR, SBR, BR or polychloroprene matrices. The HRH system is not effective with polyester fiber in any elastomeric matrix.

Initial work with the HRH system indicated that it was ineffective in highly saturated elastomers such as butyl and EPDM. Recent work, however, has shown that when sufficient zinc oxide and stearic acid (i.e., approximately 5 phr of each) are included in the formulation, good adhesion to nylon can be obtained. It is, therefore, expected that with adequate stearic acid and zinc oxide, high performance EPDM and butyl composites will be possible with the HRH system.

Applications

The most promising applications for HRH composites are those in which high modulus is required in combination with high resilience. Application examples: gaskets, motor mounts and all types of rubber springs.

The high degree of anisotropy will be useful in such applications as tubing, where swell can be minimized without decreasing elasticity.

Furthermore, since the HRH system promotes adhesion to metal and many other substrates, the HRH composites have a dual advantage of high performance and good adhesion. It is expected that these new composite materials will find their way into many diverse applications since they offer properties previously unobtainable in rubber. □