善贞
SANE ZENCHEM

better together

善贞集团
SaneZen Group

抗疲劳剂 AF2X系列在橡胶中的作用机理与应用

Mechanism & application of AF 2X series anti-fatigue agent in rubber industry

XXX

May 15, 2024

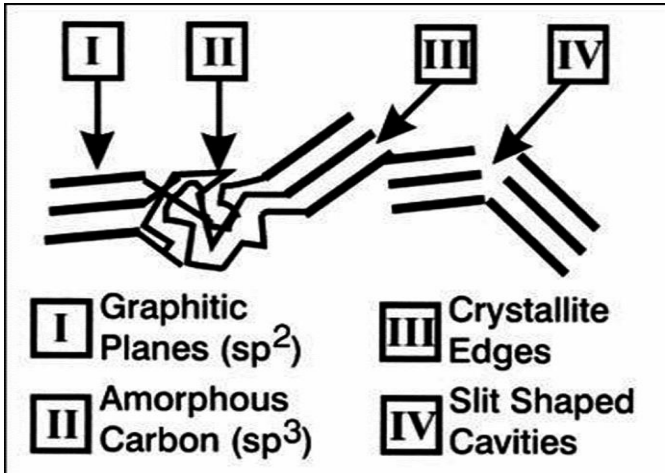
进取Enterprising　高效Efficient　共赢Win-Win

---- 橡胶解决方案的服务商

Rubber Solution Provider

Carbon black: surface structure
炭黑：表面结构

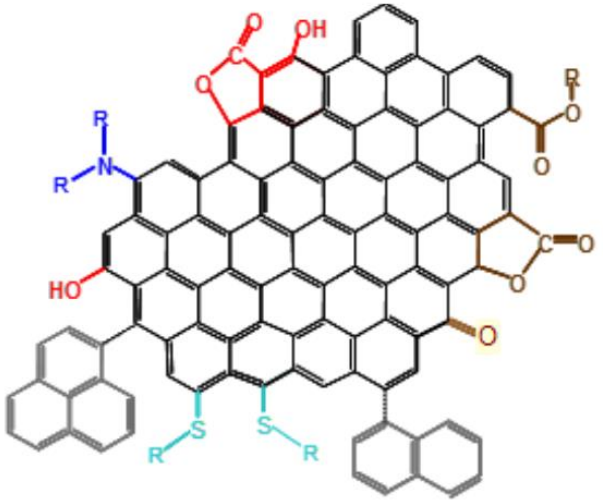
Surface structure 炭黑表面结构



Surface chemistry 炭黑表面化学

- Graphine crystalline areas石墨烯晶体区域
- Functional groups at crystal edges containing oxygen
  晶体边缘含氧的官能团

-Phenol 酚基
-Carboxyl 羧基
-Quinone 醌基
-Lactone 内酯基
-Ketones 酮基
-Lactols 乳醇基
-Aniline苯胺基



Schematic representation of carbon black surface
炭黑表面结构简图

根据炭黑表面化学性质
炭黑偶联剂

Sites of high activity: crystallite edges (III), slit shaped cavities (IV)
高活性部位：晶粒边缘（III），裂缝形空腔（IV）
Furnace carbon blacks: concentration of active sites (II-IV): 5-20%
炉黑：活性部位的含量（II-IV）：5-20%

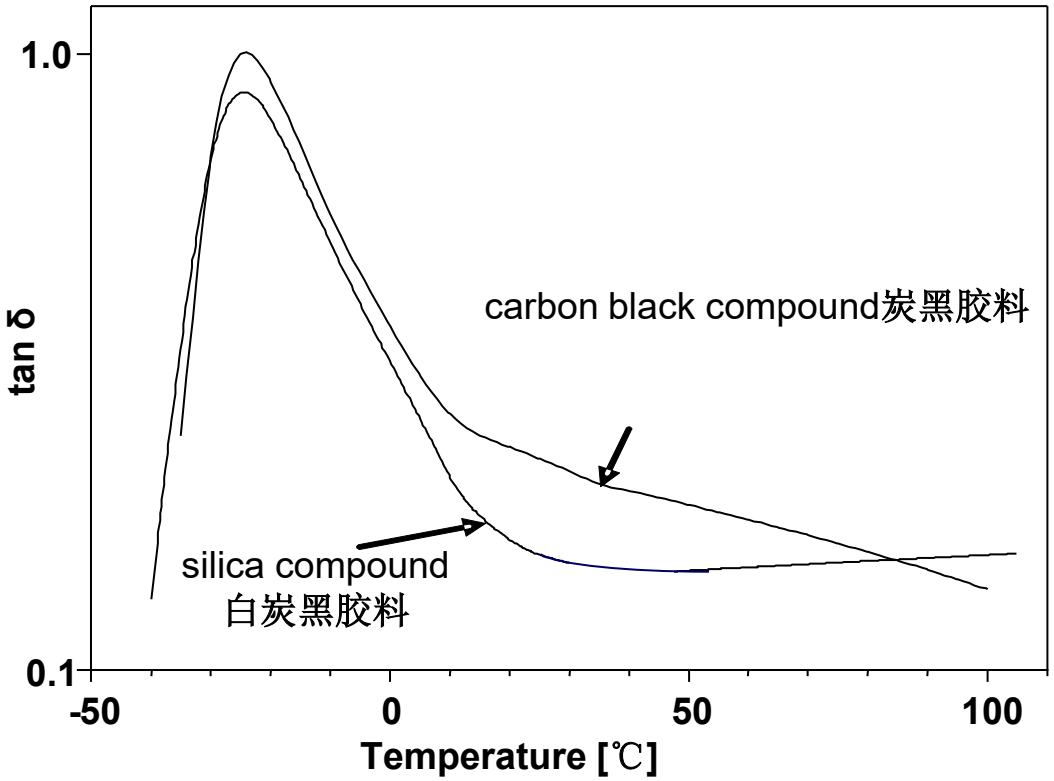
Silica vs. Carbon black: dynamic properties
白炭黑vs炭黑:动态特性

Carbon black:

Rubber chains are weakly bound to filler surface (physical adsorption)
橡胶分子链物理吸附在炭黑表面

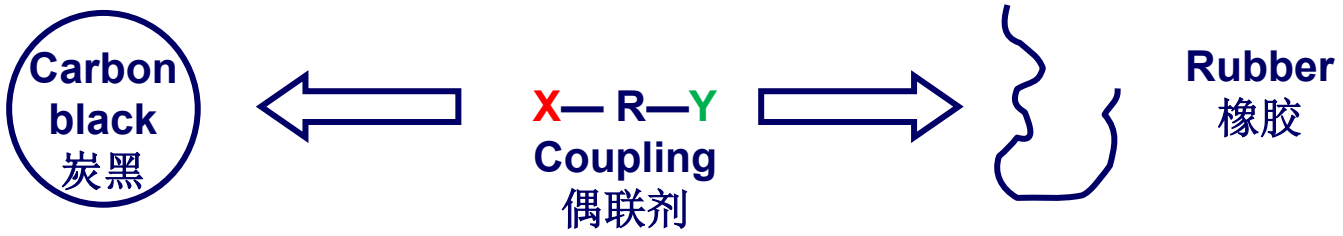
⇨ **Sliding of the chains over the surface of the filler**
橡胶分子链在炭黑表面滑移

⇨ **Energy loss** 造成能量损失



Approach: coupling rubber / carbon black
途径:偶联橡胶/炭黑

General formula: 这种偶联的“结构简式”



X:

- multifunctional covalent anchor groups
  多官能共价键基团
- multiple van der Waals interactions
  范德华力
- multiple hydrogen bonding interactions
  氢键
- multiple ionic interactions with carbon black
  离子作用力

Y:

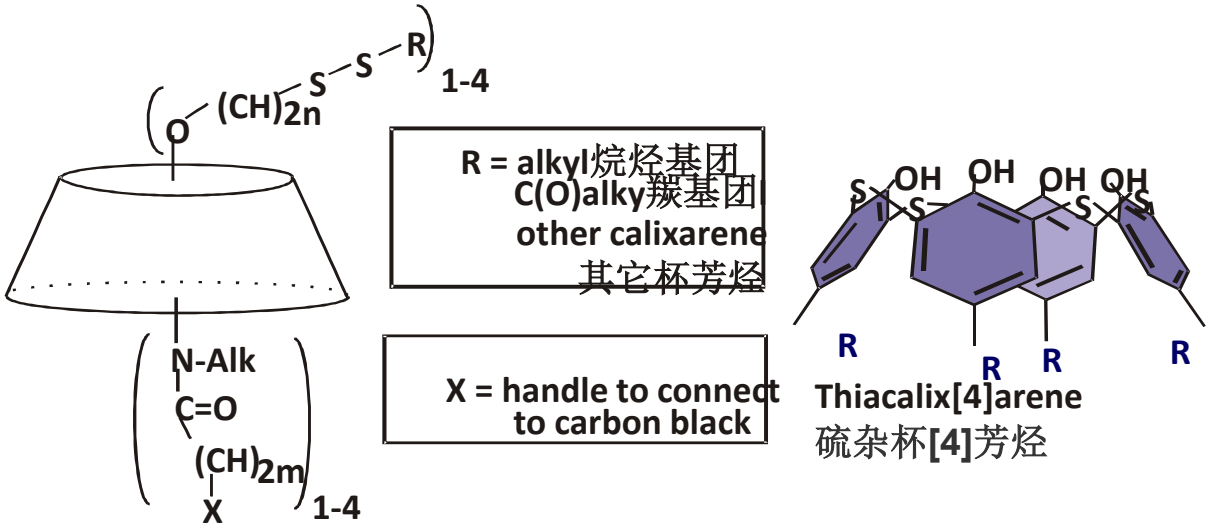
- disulphide and polysulfide moieties
- 二硫或/和多硫载体
- double bonds
- 双键
- alternative groups
  其它基团

The easier, The better

越早，越好

Approach: coupling rubber / carbon black
途径:偶联橡胶/炭黑

Y
- disulphide and polysulfide moieties二硫和多硫基团
- double bonds 含有双键
- alternative groups e.g. nitrenes 其它基团，如硝化物



Factors: 影响因素
- Number of sites at both rims
  两端活性基团数量
- Spacer lengths
  两端活性基团间隔长度
- Aromatic rings interconnected by sulfur
  通过硫黄链接的芳环种类

X
- multifunctional covalent anchor groups多官能共价靶向基团
- multiple van der Waals interactions 多个范德华作用力
- multiple hydrogen bonding interactions 多个氢键作用力
- multiple ionic interactions with carbon black 多个与炭黑之间离子作用

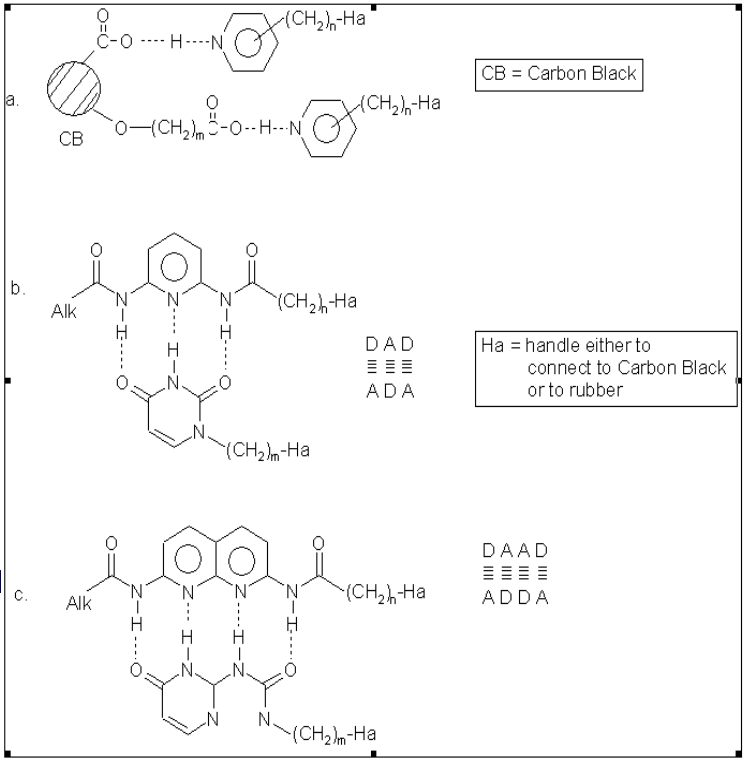
Alternative 1: coupling rubber / carbon black
备选方案1:偶联橡胶/炭黑

Y

- **disulphide and polysulfide moieties**
  二硫和多硫基团
- **double bonds** 含有双键
- **alternative groups e.g. nitrenes**
  其它基团，如硝化物

X

- **multiple hydrogen bonding interaction**
  多个氢键作用力



Alternative 2: coupling rubber / carbon black
备选方案2:偶联橡胶/炭黑

Coupling agent 炭黑偶联剂:

$X–(CH_2)_n–S–S–(CH_2)_n–X$

（其中X可以是—OH、 —NH_2、—Br）

X = OH + CB-COOH炭黑羧基 ⇨形成 ester 酯基

= NH_2 + CB-C=O炭黑羰基 ⇨形成imine 亚胺基

+ CB-COOH炭黑羧基 ⇨形成amide 酰胺基

= Br + CB-phenolic OH炭黑酚羟基 ⇨形成ether 醚基

Alternative 3: activation rubber
备选方案3:活化橡胶

Increase of the interaction between carbon black, rubber and the coupling agent by

增加炭黑、橡胶和偶联剂之间的相互作用

⇨ **Activation of the rubber:**

通过激活橡胶

Chemical modification by attachment of polar anchoring groups

通过附加极性锚定基团的化学修饰

Alternative 4: activation CB
备选方案1:偶联橡胶/炭黑

Enhanced Interaction through Surface Activation of Carbon Black

增强相互作用通过偶联剂与炭黑表面活化：

-Activation of carbon black surface:

炭黑表面活化

- **Chemical reactions**

  化学反应

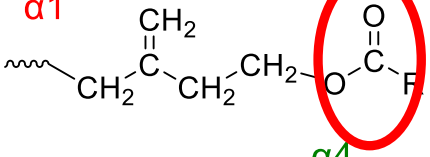
- **Physical treatments**

  物理方法

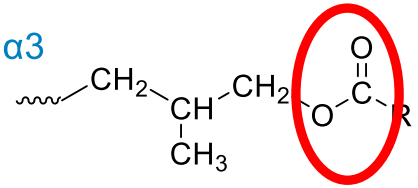
AF2X Anti-fatigue agent reduces heat generation mechanism

Natural rubber main chain and end base structure

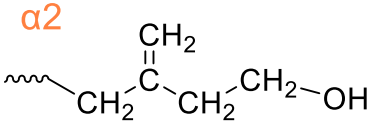
α1



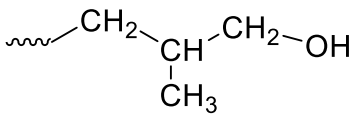
α3



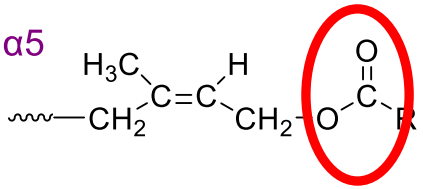
α2



α4

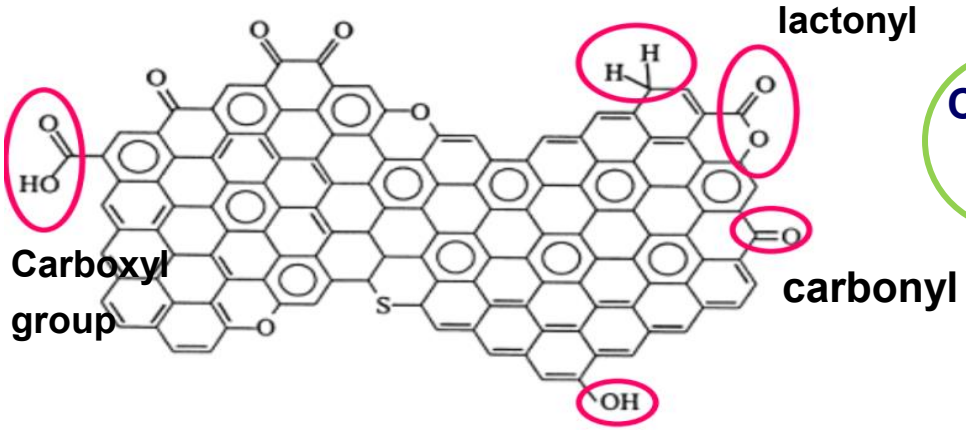


α5

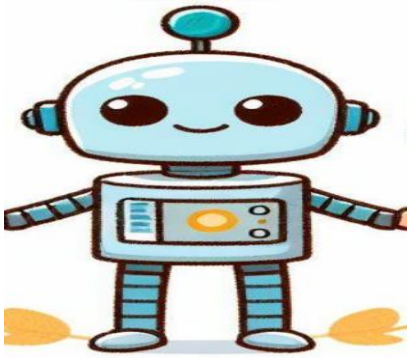


Coupling mechanism - addition reaction

Surface functional group structure of high structure carbon black



Carbon black 炭黑 X



Y Rubber 橡胶

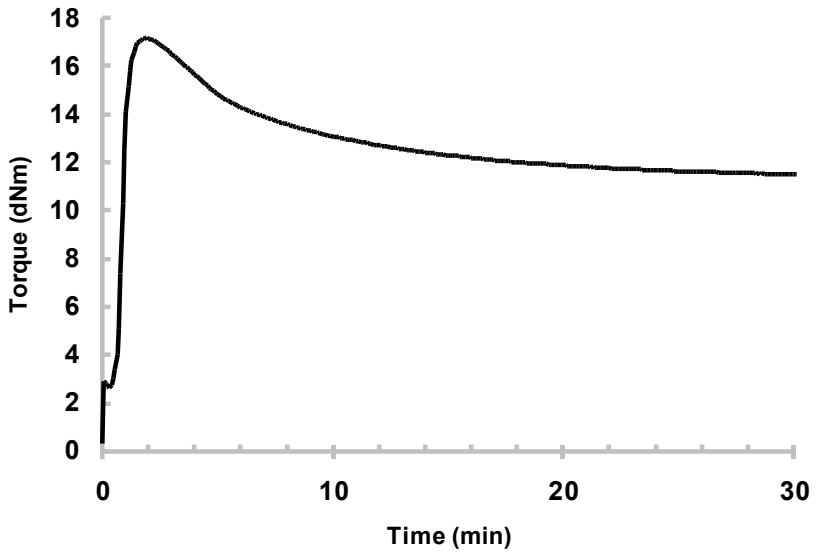
Anti-fatigue agent AF28

AF2X Anti-fatigue agent reduces heat generation mechanism

Anti-fatigue agent AF28 It is a compound containing functional groups such as hydrazide and hydroxyl group, which is specially designed for the low heat generation and fatigue resistance of natural rubber (NR) molecular chains. The complex can chemically react with the end group of NR molecular chain or the aldehyde group (C=O) on the macromolecular chain to achieve efficient chemical modification of NR molecular chain. At the same time, AF28 can also combine with functional groups on the surface of carbon black particles during the reaction with NR molecular chains, which not only reduces the free end of rubber molecular chains, but also enhances the binding force between rubber molecular chains and filler particles, and promotes the uniform dispersion of carbon black. Together, these modifications effectively reduce the internal friction of the rubber composite material, reduce the generation of heat, reduce the lag loss, and then reduce the rolling resistance of the tire, improve the tire performance.

什么是硫化返原?

What is reversion?
什么是硫化返原?

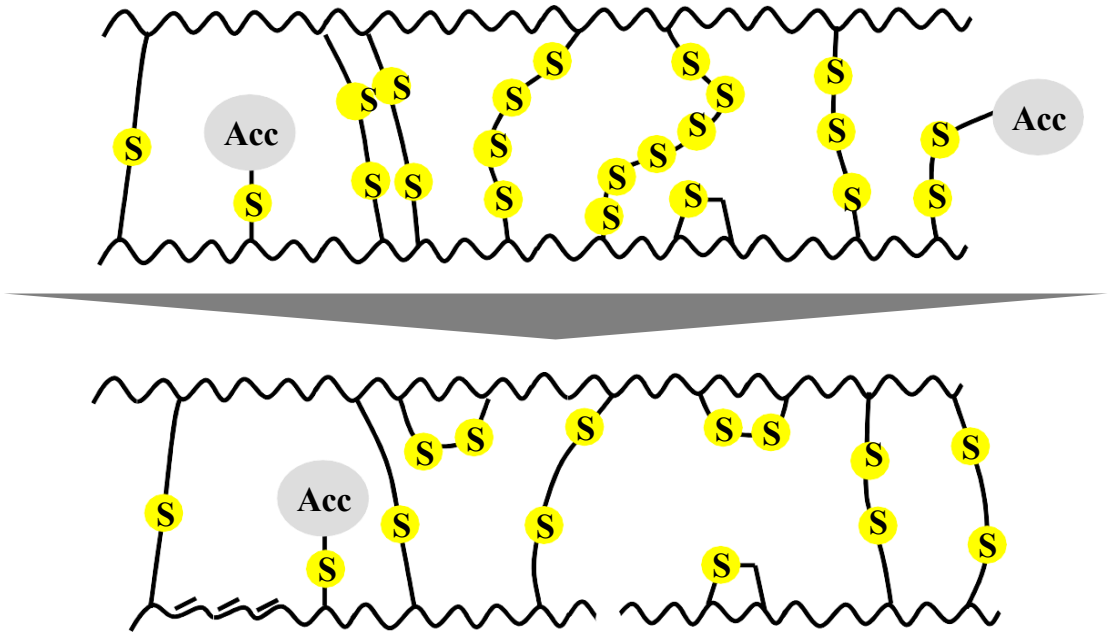


- Reduction of cross linking density during curing
- Can be seen in the rheometer
- Breaking of the polymeric chain by heat (or UV light)
- Lost of strength
- Especially NR (natural rubber) is sensitive to reversion

Reversion is a challenge in the tire industry

- High temperatures during vulcanization and use of rubber parts can cause sulfur crosslinking bonds to break.
- Polysulfur crosslinking is broken.
- The crosslinking density decreases.
- The crosslinking type changes.
- The physical properties of rubber parts change (e.g., modulus, tensile strength, elongation, fatigue behavior, heat resistance).
- **The service life of tires is reduced.**
- **Reversion leads to a reduced tire life time and reduced tire performance**

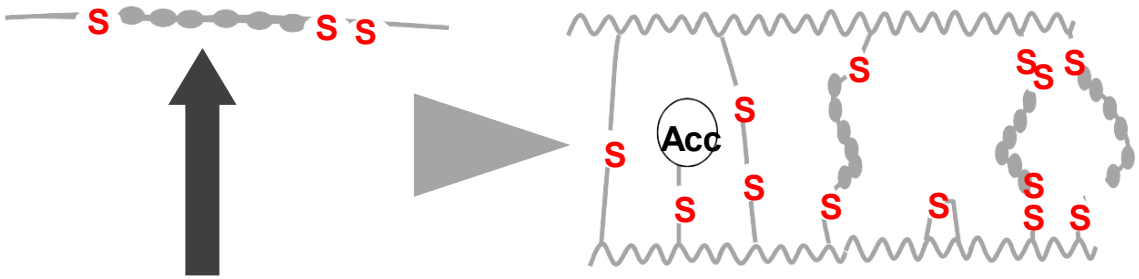
硫化橡胶交联硫化键



Anti-fatigue agent AF28 – Anti-reversion

AF28 - can reduce the degradation of polysulfide bonds due to heat, thereby improving the thermal stability of vulcanized rubber

能减少一些多硫键因热而发生的降解，从而提高硫化胶的热稳定性



Anti-fatigue agent AF28

- **Optimized tire performance with regard to reversion and tan delta at 60° C (rolling resistance)**

优化轮胎性能

硫化返原

在60° C tan delta (滚动阻力)

14

The application of anti-fatigue agent AF27 in damping products - significantly improve the damping performance

Shanghai Powerflex New Material Co., Ltd（under Sane Zen Group ）The anti-fatigue agent AF27 developed by Powerflex. Designed to improve the performance of rubber products. The reaction of surface active groups with the end groups of natural rubber molecular chains effectively optimized the dispersion of carbon black in rubber, and significantly reduced the dynamic heat generation of natural rubber carbon black system. This improvement enhances the dynamic mechanical properties of the compound, improves the heat aging characteristics of rubber products, and reduces the compression heat generation, thereby extending its service life. The appropriate use of AF27 can not only increase the hardness, elasticity and constant elongation stress of the compound, but also have no obvious effect on the tensile strength.

In shock-absorbing products, AF27 prevents vulcanizates from reverting after high temperatures or prolonged use - a condition in which physical properties decline due to degradation of the cross-linked network of vulcanizates. AF27 can slow down the degradation rate of polysulfide bonds due to increasing temperature, thereby improving the thermal stability of vulcanized rubber and extending the service life of shock absorber products.。

The application of anti-fatigue agent AF27 in damping products - significantly improve the damping performance

Main functions：

- 1. Reduce dynamic heat generation: significantly reduce hysteresis loss by changing the structure of the end of the molecular chain.
- 2. Increase elasticity: significantly improve the elasticity of rubber products.
- 3. Reduce the dynamic and stiffness ratio: optimize the effect of shock absorption products.
- 4. Prevent return phenomenon: protect vulcanized rubber to remain stable under extreme conditions.
- 5. Accelerated vulcanization: improve production efficiency.

Suggestions for use：

- Suitable for natural rubber or rubber based on natural rubber, the recommended dosage is 1~1.8 phr.
- The anti-fatigue agent AF27 must be added when mixing natural rubber NR to maximize its effect.

The application of anti-fatigue agent AF27 in damping products - significantly improve the damping performance

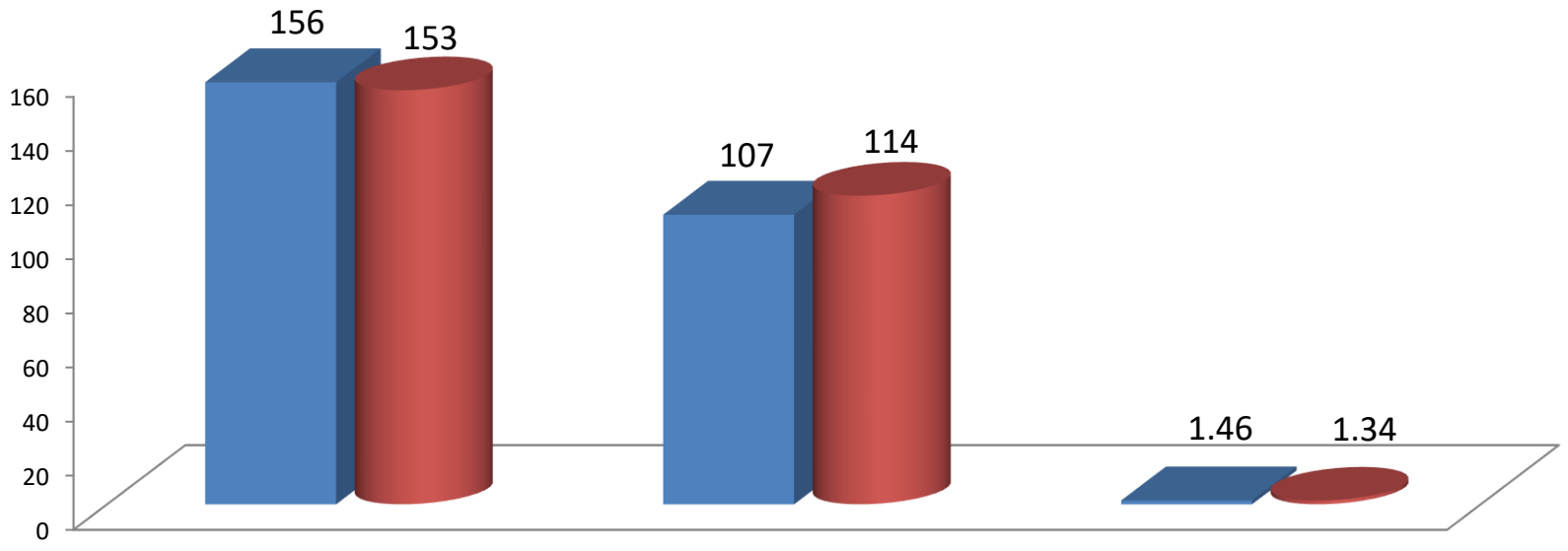
The addition of anti-fatigue agent **AF27** effectively reduces the dynamic and static stiffness ratio: improves the performance of shock absorber products.

For shock-absorbing rubber products, we compared two formulations :

Formula 1: This is the basic formula of shock-absorbing rubber products .
Formula 2: On the basis of formula 1, we added anti-fatigue agent AF27, the dosage is 1.2 phr.

The carbon black components in the formulation, including N330 and N774, are 35 phr, and the addition of anti-fatigue agent AF27 improves the dispersion of carbon black. Specifically, in rubber products, this improvement results in a lower static/static stiffness ratio (Kd/Ks). It has been reduced from 1.46 to 1.34, making it more shock absorbing. Other performance changes are minimal.

The application of anti-fatigue agent AF27 in damping products - significantly improve the damping performance



Application of anti-fatigue agent AF28 in tire - Guarantee of high performance and safety

Shanghai Powerflex New Material Co., Ltd（under Sane Zen Group）The anti-fatigue agent **AF28** developed by Powerflex effectively improves the dispersion of carbon black, and the highly active groups on its surface can react with the corresponding groups at the end of the natural rubber molecular chain, thereby significantly reducing the dynamic heat generation of the natural rubber carbon black system. Performance, it can improve the dynamic mechanical properties of the rubber and reduce rolling resistance. It can improve the heat aging resistance of the tire, reduce compression heat generation, and extend the service life. Adding an appropriate amount of anti-fatigue agent **AF28** can improve the hardness, elasticity, and elongation of the rubber. stress without significantly changing the tensile strength.

At the same time, it can prevent the vulcanized rubber from returning to its original state after high temperature or long-term use, that is, the cross-linked network of the vulcanized rubber is degraded, resulting in a decrease in physical properties. The anti-fatigue agent **AF28** can reduce the thermal degradation of some polysulfide bonds. Degradation occurs, thereby improving the thermal stability of the vulcanized rubber.

The use of anti-fatigue agent **AF28** is crucial to improving the quality, safety and life of tires.

Application of anti-fatigue agent AF28 in tire - Guarantee of high performance and safety

Main function：

- 1. Reduce heat generation: the end of the molecular chain is modified, the hysteresis loss of vulcanized rubber is improved significantly, and the dynamic heat generation is reduced.
- 2. Improve elasticity: significantly improve rubber elasticity.
- 3. Reduce rolling resistance: It can improve the dynamic mechanical properties of the compound and reduce rolling resistance.
- 4. Prevent vulcanization return: Prevent vulcanized rubber from returning after high temperature or long time use.
- 5. Speed up vulcanization: improve production efficiency.

Suggestions for use:

1. Suggestions for use: Only applicable to natural rubber or rubber based on natural rubber, the recommended dosage is 1~1.6 phr.

2. It is necessary to use natural rubber NR as raw material to add anti-fatigue agent AF28 in a stage of mixing to effectively exert the maximum effect.

Application of anti-fatigue agent AF28 in tire - Guarantee of high performance and safety

No.	Raw material	Formula 1 (None)	Formula 2 (With anti-fatigue agent)
1	SCR 10	100	100
2	N234	47	47
3	ZnO	3	3
4	SA	3	3
5	Wax	1	1
6	4020	1.2	1.2
7	RD	1	1
8	S	1.5	1.5
9	NS	1.1	1.1
10	AF28		1
Total:		158.8	159.8

Test	Formula 1	Formula 2
ML(dN.m)	1.92	2.56
MH(dN.m)	18.1	17.01
T10 (min)	3.66	3.26
T50 (min)	4.91	3.88
T90 (min)	10.21	7.21
TS2 (min)	3.92	3.35

Vulcanization condition of rubber:
151℃ ×60min
Test standard: GB/T 16584-1996

Application of anti-fatigue agent AF28 in tire - Guarantee of high performance and safety

Test		Formula 1 (None)	Formula 2 (With anti-fatigue agent)	Conditions of vulcanization	Standard
Mooney	ML(1+4)100℃	62	75	100℃	ASTM D1646
Hardness	Shore A	65	66	151℃*30min	ASTM D2240
M100%	Mpa	2.9	3		ASTM D412
M300%	Mpa	14.8	15.5		
Tensile Strength	Mpa	33.3	32.9		
Elongation	%	551	529		
Tear Strength	m/kN	95	94		ASTM D624
Rebound%		43	49	151℃×30min	GB/T 1681-2009
Rebound% Tear Strength100℃×48h		48	51		
Worn volume/cm3		0.141	0.144	151℃×30min	ISO-23337
E'/MPa	0℃	22.01	17.67	DMA 151℃×30min	ISO-23337
	60℃	12.45	10.57		
tan σ	0℃	0.129	0.126		
	60℃	0.098	0.08		
	Improvement rate%	100	81.6		

如需了解更多产品信息，请联系我们区域的专业销售工程师，访问善贞官网 www.sanezen.com 或善贞1688电商平台。

区域范围	销售工程师	联系方式（微信同号）
上海/湖北/苏州(昆山 太仓 常熟 张家港) 东北三省	刘经理	152 0177 8745
江苏北/河北/陕西/ 河南/山东	汪经理	158 0215 3364
北京	章经理	138 1770 6068
安徽/福建/浙江（除宁波、台州、杭州）	汪经理	177 1768 9203
无锡/南京/青岛	毕经理	138 1652 3748
台州 /杭州/苏州(吴江 相城)/广东/天津	汪经理	158 0046 9072
江西/安徽/福建/浙江（宁波）	鲍经理	1367 164 6628
四川/重庆	汪经理	139 1804 7582
湖南/贵州/广西/镇江/常州	李经理	182 1748 5743
海外	陈经理	136 7164 1995

交流微信

专业交流
技术探讨
合作洽谈

高端 橡胶圈

行业交流
技术答疑
市场分析

善贞 公众号

产品咨询
行业动态
解决方案