Some New Chemicals for Rubber and Their Reactivities as Free Radical Sources

By

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The present paper is concerned with investigations about some new chemicals for rubber processing. The actions of the chemicals were classified into several types according to their selective activities. Chemicals having the tendency to abstract hydrogen atom from rubber molecules act as crosslinking agents or peptizers according to the nature of the radical produced and to the presence of oxygen. Benzoyl disulfide and diazothioether were found to be new vulcanizing agents and the quaternary ammonium salts of the aromatic series, sulfinic acids and alkyl nitrites were new peptizers for rubber. The chemicals composed of stable radical species acting as acceptors for sulfur radicals were found to be anti-scorch agents. Chloro- or nitroso-compounds of imide, imine, alcohol, or mercaptan were found to have such characters. Aliphatic quaternary salts producing radicals with moderate activity on heating may open the sulfur rings. The vulcanization characteristics of some synthetic rubbers were found to be improved by using of some modifiers such as thioacetamide, trichloroisocyanuric acid, and trichloro-melamine.
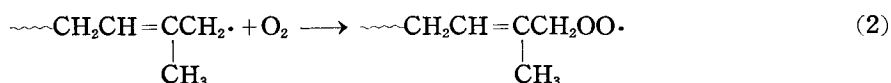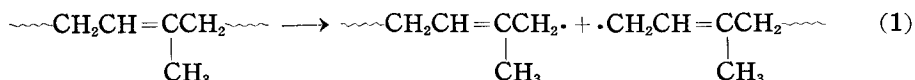
Introduction

Since Goodyear's discovery of vulcanization, rubber chemistry has developed by the application of a great number of other chemicals such as organic vulcanization accelerators, antioxidants, mastication accelerators and anti-scorch agents. This article deals with the relationships among reagents applied to rubber in order to discover new rubber chemicals. Thiazoles or thiocarbamates that have a $\begin{smallmatrix} -N \\ -S \end{smallmatrix}\!\!>\!\!C\text{-SH}$ or $\begin{smallmatrix} -NH \\ -S \end{smallmatrix}\!\!>\!\!C\text{=S}$ structure as their terminal group respectively exhibit excellent acceleration characteristics for vulcanization, but arylthiols such as thiophenol that have the –SH group are well known as active peptizers of rubber. From such facts the question arises as to why the thiol compounds attached to a C=C bond such as the thiophenols act as peptizers, while the thiol compounds attached to a C=N or C=S bond such as the thiazoles or thiocarbamates act as vulcanization accelerators. For facilitating research on new chemical for rubber,
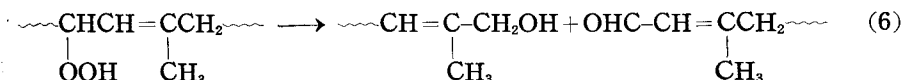

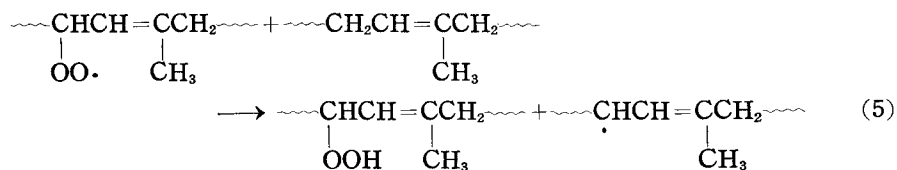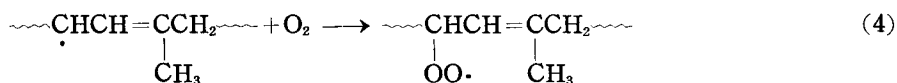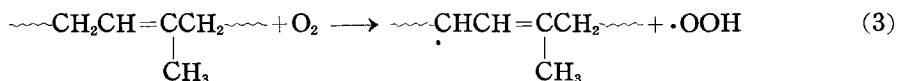
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it may be very important to elucidate the mode of action and reactivities of chemicals.

I.　The Mode of Reaction of Peptizers

It has long been known that the mastication of rubber is influentially affected by the presence of oxygen. Watson interpreted the mastication in terms of the radical mechanism, that is, oxygen acts as the acceptor for rubber radicals produced by a mechanical breakdown of the rubber molecule on mill as follows[2],

$$\sim\sim CH_2CH=CCH_2\sim\sim \longrightarrow \sim\sim CH_2CH=CCH_2\cdot + \cdot CH_2CH=CCH_2\sim\sim \qquad (1)$$
$$\overset{|}{CH_3} \qquad\qquad \overset{|}{CH_3} \qquad\qquad \overset{|}{CH_3}$$

$$\sim\sim CH_2CH=CCH_2\cdot + O_2 \longrightarrow \sim\sim CH_2CH=CCH_2OO\cdot \qquad (2)$$
$$\overset{|}{CH_3} \qquad\qquad\qquad \overset{|}{CH_3}$$

In the absence of oxygen or other acceptor, the rubber radical reacts with other rubber molecules or radicals to produce cross-linking or recombination. Watson proposed that other radical acceptors such as quinone, phenol or nitrophenol would be effective masticators by their protection of rubber radicals. In this case the rate of matication is thought to be determined by the mechanical breaking of the rubber molecule which proceeds most effectively at lower temperatures. In contrast with the so-called "cold mastication" mechanism proposed by Watson, we have suggested an alternative process for high temperature mastication, i.e., that on a hot roll mill or closed-type mastication[1]. In the latter case the reaction may proceed through the auto-oxidation mechanism as follows,

$$\sim\sim CH_2CH=CCH_2\sim\sim + O_2 \longrightarrow \sim\sim\underset{\cdot}{C}HCH=CCH_2\sim\sim + \cdot OOH \qquad (3)$$
$$\overset{|}{CH_3} \qquad\qquad\qquad \overset{|}{CH_3}$$

$$\sim\sim\underset{\cdot}{C}HCH=CCH_2\sim\sim + O_2 \longrightarrow \sim\sim CHCH=CCH_2\sim\sim \qquad (4)$$
$$\overset{|}{CH_3} \qquad\qquad\qquad \overset{|}{OO\cdot}\ \overset{|}{CH_3}$$

$$\sim\sim CHCH=CCH_2\sim\sim + \sim\sim CH_2CH=CCH_2\sim\sim$$
$$\overset{|}{OO\cdot}\ \overset{|}{CH_3} \qquad\qquad \overset{|}{CH_3}$$
$$\longrightarrow \sim\sim CHCH=CCH_2\sim\sim + \sim\sim\underset{\cdot}{C}HCH=CCH_2\sim\sim \qquad (5)$$
$$\overset{|}{OOH}\ \overset{|}{CH_3} \qquad\qquad \overset{|}{CH_3}$$

$$\sim\sim CHCH=CCH_2\sim\sim \longrightarrow \sim\sim CH=C-CH_2OH + OHC-CH=CCH_2\sim\sim \qquad (6)$$
$$\overset{|}{OOH}\ \overset{|}{CH_3} \qquad\qquad \overset{|}{CH_3} \qquad\qquad \overset{|}{CH_3}$$

where oxygen acts not only as the radical acceptor in reaction (4) but also as the radical initiator in reaction (3). From the above consideration, other useful peptizers than the acceptors proposed by Watson will be suggested, that is the

initiator type peptizer. For example butylnitrite was found to be an effective peptizer when it was used in the presence of oxygen. If oxygen is absent, the yellow rubber nitrite can be obtained, and the viscosity of a solution of rubber nitrite decreases markedly when the solution is exposed to an oxygen atmosphere. Benzoyl peroxide is another example and is useful as a non-sulfur vulcanizer when used in the absence of oxygen. However, the rubber compounded with peroxide is found to suffer from oxidative degradation when the rubber compound

Table I. Activities of various peptizers.

Chemicals	$\dfrac{\text{moles}}{100\,\text{g rubber}}$	Wt. %	Preheating condition	Relative plasticity	Mixing condition	Plasto-meter
C_6H_5SH	0.68×10^{-2}	0.5	80°C×50′	1.75*	50–54°C×4 min.	Goodrich at 80°C
			80°C×100′	2.02*		
$(C_6H_5)_3CCl$	0.68×10^{-2}	1.27	80°C×50′	1.98*	,,	,,
			80°C×100′	2.12*		
$(p\text{–}CH_3C_6H_4)_3C\cdot Cl$	0.68×10^{-2}	1.45	80°C×50′	2.36*	,,	,,
			80°C×100′	2.18*		
C_6H_5SH	1×10^{-2}	—	100°C×30′	1.67*	—	Goodrich at 80°C
$p\text{–}CH_3\text{–}C_6H_4\text{–}SO_2H$	1×10^{-2}	—	100°C×30′	1.90*	—	,,
RPA No. 2	—	2	100°C×4′	1.74**	45–50°C×7 min.	Mooney at 100°C
$p\text{–}NO_2\text{–}C_6H_4\text{–}N=N\text{–}S$ $\text{–}(p\text{–}CH_3)C_6H_4$	—	2	100°C×4′	1.58**	,,	,,
$p\text{–}Cl\text{–}C_6H_4\text{–}N=N\text{–}S$ $\text{–}(p\text{–}CH_3)C_6H_4$	—	2	100°C×4′	1.67**	,,	,,
$(CH_4)_2N\text{–}C_6H_5$	1×10^{-2}	—	100°C×4′	1.04**	75–80°C×13 min.	Mooney at 100°C
$C_6H_5CH_2Cl$	1×10^{-2}	—	100°C×4′	1.02**	,,	,,
$\overset{+}{[C_6H_5\text{–}N(CH_3)_2]}\,Cl^-$ $\overset{\|}{CH_2C_6H_5}$	1×10^{-2}	—	100°C×4′	1.17**	,,	,,
$\overset{+}{[C_6H_5CO\text{–}N(CH_3)_2]}\,Cl^-$ $\overset{\|}{C_6H_5}$	1×10^{-2}	—	100°C×4′	1.22**	,,	,,
$\overset{+}{[p\text{–}Cl\text{–}C_6H_4\text{–}NHCH_3]}\,Cl^-$ $\overset{\|}{CH_3}$	1×10^{-2}	—	100°C×4′	1.26**	,,	,,
$C_6H_5SO_2Cl+(CH_3)_2NC_6H_5$	1×10^{-2}	—	100°C×4′	1.29**	,,	,,

* [Relative plasticity]$=\dfrac{\text{(Goodrich Plasticicy of Rubber mixed with Peptizer)}}{\text{(Goodrich Plasticity of Rubber)}}$.

** [Relative plasticity]$=\dfrac{\text{(Mooney Viscosity of Rubber)}}{\text{(Mooney Viscosity of Rubber mixed with Peptizer)}}$.

is heated while exposed to oxygen. We have found organic sulfinic acid[4], triphenylmethyl chloride[5] butyl nitrite, N-nitrosodiphenylamine[3] and some quarternary ammonium salts[6] to be effective peptizers capable of oxidizing rubber. Table I shows the activities of various peptizers that were developed in our laboratory. In the case of initiator type peptizers, oxygen is necessary to stop the radical chain. Since the rate-determing step may probably be a reaction of hydrogen abstraction, the activity of these peptizers will be due to the ability for hydrogen abstraction of the radicals they produce. Peptizers lower the initiation temperature for the auto-oxidation of rubber, although the temperature is always higher than that which is suitable for mechanical mastication. It is noteworthy that auto-oxidative mastication is sometimes more effec-

Fig. 1. Classification of chemical mastication and mechanical mastication.

tive than cold mastication. Fig. 1 illustrates the behavior characteristics of both types[1] of peptizers.

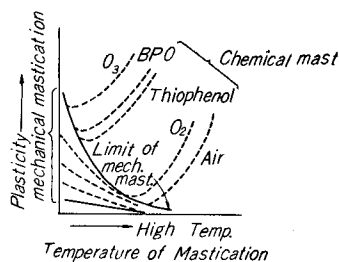## II. Cross-Linking Agent or Non-Sulfur Vulcanizer

Since the peptization of auto-oxidation involves the abstraction of hydrogen atoms from rubber molecules, these peptizers act also as cross-linking agents when they are used in the absence of oxygen. However, the most effective cross-

Table II. Physical properties of cross-linked rubber by p,p′–disubstituted benzoyl disulfide.

Recipe: Natural rubber : 100, benzoyl disulfide ; 0.032 moles, zinc oxide ; 10, stearic acid ; 1, light calcium carbonate ; 30, cure temperature ; 145°C.

Vulcanizates	Cure time (min)	100% Modulus (Kg/cm²)	Tensile strength at break (Kg/cm²)	Elongation (%)	Hardness (Shore)
p,p′–CH₃O–BDS	15	7.2	165	705	38
	30	7.9	152	633	40
p,p′–CH₃–BDS	20	5.4	128	780	34
	40	5.8	124	740	35
BDS	20	5.0	84	740	32
	40	5.3	85	720	33
p,p′–Cl–BDS	20	7.3	150	710	40
	40	7.7	144	685	40
p,p′–NO₂–BDS	30	3.0	34	700	20
	60	3.0	—	—	23

(BDS indicates benzoyl disulfide)

linking agents will be those reagents which produce the more active radicals on thermal decomposition. Benzoyl disufide[10] is one such cross-linking agent. It is interesting that it has a similar chemical structure to that of benzoyl peroxide or tetramethylthiurum disulfide, the latter of which is wellknown as a non-sulfur vulcanizer. Table II shows the vulcanizing activity of benzoyl disulfide derivatives[10]. The effects of the negative substituents on benzoyl disulfide follow Hammet's rule.

Diazothioether is interesting as a powerful cross-linking agent, although it acts as a peptizer when it is used in an atmosphere of air[11]. The substance consists of two components, i.e. an azo-radical and a thio-radical, the former may be the initiator and the latter the acceptor, when it decomposes on heating as follows;

$$X-\langle\;\rangle-N=N-S-\langle\;\rangle-Y \longrightarrow X-\langle\;\rangle\cdot + N_2\uparrow + \cdot S-\langle\;\rangle-Y.$$
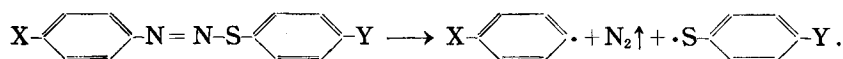
III. Accelerators for Sulfur Vulcanization

The usual accelerators have been thought to facilitate the opening of the sulfur ring to produce atomic or ionic sulfur. The sulfur molecule is thought to have a ring structure, which decomposes at elevated temperatures to yield atomic sulfur or its polymer.
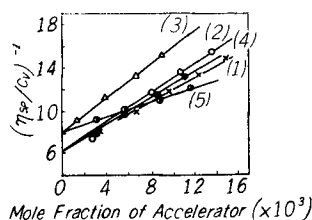

Fig. 2. Relations between equilibrium viscosity and concentration of vulcanization accelerator.

(1) Dibenzothiazolyl disulfide, 0.3.
(2) N–Cyclohexyl-2-benzothiazolyl sulfeneamide, 0.2.
(3) Tetramethylthiuram disulfide, 0.5.
(4) Tetramethylthiuram monosulfide, 0.2.
(5) Acetaminophenyl disulfide, 0.8.
(Number indicates grams of reagent per 9 g sulfur.)

$$S_8 \text{ ring} \rightleftharpoons \cdot S_8 \cdot \rightleftharpoons \cdot (S_8)_x \cdot$$

The reaction is reversible and the degree of polymerization of sulfur depends upon the reaction temperature. The authors believe that it acts as an organic accelerator not only by initiating such ring cleavage, but also as a transfer agent for the polymerization of a sulfur chain. Molten sulfur polymerizes more rapidly in the presence of an accelerator, and the equilibrium viscosity of molten sulfur decreases with an increasing concentration of an accelerator according ot the following equation[8],

$$(\eta_{sp}/C_v)^{-1} = \text{const} + (k_t/k_p)(A)/(S_8)$$

where C_v is the volumetric concentration of the vulcanization accelerator, η_{sp} is the specific viscosity of the molten sulfur mixed with the accelerator, (A) and

(S_8) are the concentrations of the accelerator and sulfur respectively.
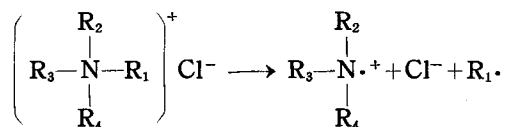
Some vulcanizing accelerators of new types were studied in our laboratory, one of which is the quarternary ammonium salt of aliphatic amine such as is shown in Table III[7].

Table III. Effectiveness of quarternary ammonium salts as vulcanization accelerators.

Recipe: Natural rubber; 100, zinc oxide; 5, ammonium salt; 0.005 moles, sulfur; 3, cure temperature; 144-145°C.

Ammonium salt	Cure time (min)	Tensile strength at break (Kg/cm²)	Elongation (%)	Hardness (Shore)
Lauryldimenthylbenzyl ammoniumchloride	5	203	865	32
	10	232	760	37
Lauryltrimethyl ammoniumchloride	5	146	845	28
	10	182	815	33
p–Chlorobenzyldiethyl ammoniumhydrochloride	10	80	915	25
	20	178	910	28
p–Chlorobenzyltriethyl ammoniumchloride	10	54	820	24
	20	125	885	27
Benzylpyridinum chloride	5	107	835	27
	10	155	810	30

Quarternary ammonium salts have been known as active surface agents useful for the preparation of colloidal calcium carbonate, but these salts possess vulcanizing activity. The above experiment illustrates an ability of the compound which is not an action as a surface agent but as an ordinary vulcanizing agent. Quarternary salts were found to decompose homolytically[21] and the radicals produced may have an initiating action on the decomposition of the sulfur ring.
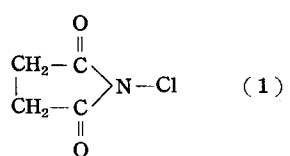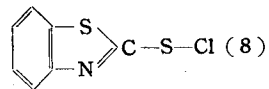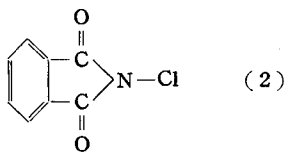
$$\left(\begin{array}{c} R_2 \\ | \\ R_3-N-R_1 \\ | \\ R_4 \end{array} \right)^+ Cl^- \longrightarrow \begin{array}{c} R_2 \\ | \\ R_3-N\cdot^+ +Cl^- +R_1\cdot \\ | \\ R_4 \end{array}$$
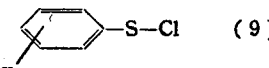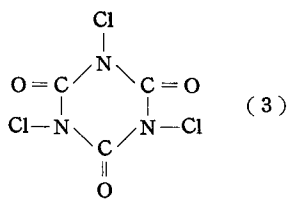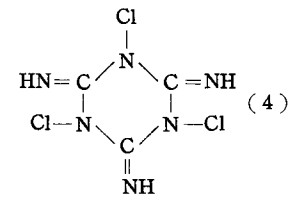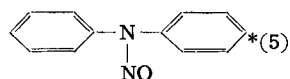
It is interesting that the salts having an aromatic group as a component are not effective in vulcanization but have a peptizing action on rubber. Such differing behavior as this may be attributed to the stability of the radicals derived from the quarternary salt, which is probably greatly stabilized by the phenyl group attached to the nitrogen atom.

It was found that some promoters of vulcanization have no activity as vulcanizing accelerators by themselves but exhibit such effects when used together with other accelerators. Thiobenzamide and methyl xanthogen amide are known to be the most effective promoters[9].

IV. Some New Anti-Scorch Agent

Little has been known about anti-scorch agents apart from N-nitrosodiphenylamine. Recently trichloromelamine was found to have an anti-scorching action but is not used because of its explosive nature[22]. N-Chloro derivatives of amides were found to be usable as non-staining anti-scorch agents in our laboratory. Compounds such as N-chloro succinimide[12], N-chlorophthalimide[12], dichlorourea[13] and trichloroisocyanuric acid[21], having the structure of $-\underset{\underset{O}{\|}}{C}-\underset{|}{N}-Cl$ similar to that

of $-\underset{\underset{NH}{\|}}{C}-\underset{|}{N}-Cl$ in N-chloromelamine, exhibit excellent anti-scorching action. More-

Table IV. Some new anti-scorch agents.

	$X = \underset{|}{C} - \underset{|}{N} \cdot$	$X = \underset{|}{C} - O \cdot$	$X = \underset{|}{C} - S \cdot$
Cl·	$\begin{matrix} CH_2-C \\ | \\ CH_2-C \end{matrix} \!\!\! >\!\! N-Cl$ (1)	$(CH_3)_3C-O-Cl$ (6)	benzothiazole $>C-S-Cl$ (8)
	phthalimide $>N-Cl$ (2)		$X-\!\!\!\bigcirc\!\!\!-S-Cl$ (9) $\begin{pmatrix} x = o-NO_2 \\ o-COOH \\ p-CH_3 \\ p-Cl \end{pmatrix}$
	$\begin{matrix} & Cl & \\ & | & \\ & N & \\ O=C & & C=O \\ Cl-N & & N-Cl \\ & C & \\ & \| & \\ & O & \end{matrix}$ (3)		$Cl_3C-S-Cl$ (10)
	$\begin{matrix} & Cl & \\ & | & \\ & N & \\ HN=C & & C=NH \\ Cl-N & & N-Cl \\ & C & \\ & \| & \\ & NH & \end{matrix}$ (4)		
NO·	$\bigcirc\!\!-N-\!\!\bigcirc$ *(5) $\underset{NO}{|}$	$C_5H_{11}O-NO$ (7)	$(CH_3)_3C-S-NO$ (11)

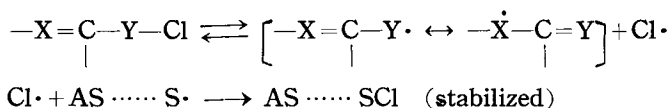* N-Nitrosodiphenylamine is one of commercial anti-scorch agents.

over, O-chloro[14] and S-chloro[15-17] or O-nitroso[15] and S-nitroso[15] derivatives were also found to be effective. Tables IV and V summarize the compounds studied.

Table V. Activities of various agents refered in table IV.

Recipe: Natural rubber, 100; zinc oxide, 5; stearic acid, 1; sulfur, 3; mercaptobenzothiazole, 0.4; hexamethylenetetramine, 0.4.

No.	Chemicals	Weight parts per 100 g rubber	Relative scorch time
(1)	N-Chlorosuccinimide	0.2	2.11
(2)	N-Chlorophthalimide	0.34	2.03
(3)	Trichloroisocyanuric acid	0.25	1.04
		0.35	2.00
(4)	Trichloromelamine (25%)	0.5	2.35
(5)	N-Nitrosodiphenylamine	0.5	1.95
(6)	t-Butyl hypochlorite	0.2	1.33
		0.6	1.69
		1.0	2.36
(7)	n-Amylnitrite	0.8	2.04
(8)	Benzothiazolylsulfenyl chloride	0.003 moles	1.73
(9)	o-Nitrophenylsulfenyl chloride	0.003 moles	3.01
	o-Carboxyphenylsulfenyl chloride	0.003 moles	2.20
	Phenylsulfenyl chloride	0.003 moles	1.38
	p-Methylphenylsulfenyl chloride	0.003 moles	1.23
	p-Chlorophenylsulfenyl cnloride	0.003 moles	1.22
(10)	Thiocarbonyl perchloride	0.003 moles	6.33
(11)	t-Butyl thionitrite	1.8	1.71

It is noteworthy that these compounds have the common structures of $-X=\overset{|}{C}-Y-Cl$ or $-X=\overset{|}{C}-Y-NO$, where X may be C or N and Y may be N, O or S. Compounds having such a structure tend to decompose to give NO· or Cl·, because the radicals produced have the stable resonating structure of $-X=C-\overset{|}{Y}·$ or $-\overset{·}{X}-\overset{|}{C}=Y$, except for tert-butyl compounds which have a stable radical component instead of a conjugated component. These facts in dicate that anti-scorch agents must decompose at high temperature to give rise to Cl· or NO· radicals which combine with sulfur atoms or radicals to stop the vulcanization.

$$-X=\overset{|}{C}-Y-Cl \rightleftarrows \left[-X=\overset{|}{C}-Y· \leftrightarrow -\overset{·}{X}-\overset{|}{C}=Y\right]+Cl·$$

$$Cl·+AS\cdots\cdots S· \longrightarrow AS\cdots\cdots SCl \quad (stabilized)$$

Thiocarbonyl perchloride (Cl₃CSCl) was found to be the most effective anti-scorch

agent and is easily prepared from carbon disulfide and chlorine. It has better antioxidizing properties than the vulcanizate compounded with N-nitroso diphenylamine as shown in Table VI[17]. N-Chloro amides or imides are sparingly soluble, but their affinity for rubber was improved by using N-chloro derivatives of the condensation product of maleic imide and tung oil[13].

Table VI. Property of vulcanizate compounded with anti-scorch agent.

Vulcanizate	Cure time (min)	Before aging			After aging	
		Tensile strength at break	Elong-ation	Hard-ness	Tensile strength	Elong-ation
Control	7	182 kg/cm²	840%	31	107 kg/cm²	615%
	10	184	805	34	103	750
	15	209	800	36	94	695
	25	277	757	41	99	635
TPC* 0.5 PHR	10	161	868	31	69	790
	15	200	855	35	87	740
	25	253	798	39	109	705
	40	263	760	42	67	595
NDA** 0.5 PHR	10	189	810	34	10	470
	15	219	815	36	23	530
	25	249	765	42	28	525
	40	275	707	45	21	325

* Thiocarbonyl perchloride
** N-Nitrosodiphenlamine

V. Modification for Butyl and Styrene-Butadiene Rubber

In order to improve the vulcanization character of butyl rubber, quinone dioximes have been proposed commercially. Trichloromelamine and trichloroisocyanuric acid were also found to be effective as promoters in our laboratory when used in the presence of carbon black[18]. The preparation of chlorinated butyl rubber has recently been claimed in a Patent by the Esso Research Laboratory[23]. In this patent the chlorination is carried out by using sulfuryl chloride in solution, but our study indicates that the chlorination of butyl rubber on a mixing roll is more practical[19].

SBR is also improved in its vulcanizable character by pretreatment in hexane solution with a small amount of thioacetamide initiated by organic peroxide[20]. The modified SBR has a high modulus and tensile-strength twice that of the original one[20] (cf. Fig. 3).
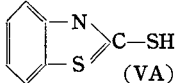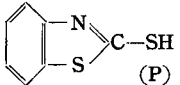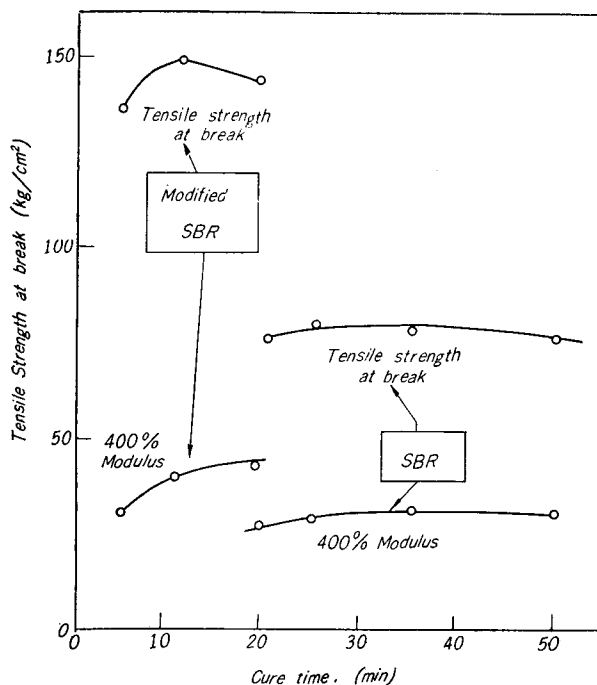
Fig. 3. Comparison of the physical properties between modified
        SBR and unmodified one.
Recipe : Rubber, 100 ; stearic acid, 1 ; sulfur, 2.5 ; ppt. -CaCO₃,
         100 ; zinc oxide, 5 ; cumarone resin. 5 ; accelerator DM,
         1.0 ; accelerator D, 0.3.

VI. Discussion on the Relationships among Cross-Linking
Agents, Vulcanization Accelerators, Anti-Scorch Agents and Peptizers

As mentioned in the first chapter the actions of reagents are classified into
several types according to the selective activity of the reagent ; cross-linking and
peptization are caused by hydrogen abstraction from the rubber molecule, and the
unstable radicals produced from reagents having great affinity to the hydrogen
atom may be suitable as an initiator for these reactions.   These compounds may
involve O-, S- and N-radical components. The activity of radicals depend also
upon their stability.   Generally speaking the more unstable radicals will act as
initators and induce cross-linking, while moderately unstable radicals act as chain
transfer agents and are suitable as peptizer with the co-operation of oxygen.
Organic peroxide and quarternary salts of the aliphatic series belong to the former
and thiophenol, sulfinic acid, alkylnitrite and quarternary salt of aromatic series
belong to the latter category. Reagents consisting of stable radical components
will act as radical acceptors, which will be suitable as anti-scorch agents. Chloro-

Table VII. Classification of chemicals on rubber: $Z-\underset{Y}{\overset{\|}{C}}-X\cdot$ (P, Peptizer; AS, Antiscorch agent; A, Vulcanization accelerator; C, Nonsulfur vulcanizer; AO, Antioxant; VP, Vulcanization promoter; φ, Phenyl; R, Alkyl).

$Z-\underset{Y}{\overset{\|}{C}}$ / $-X\cdot$	$Z-\underset{C}{\overset{\|}{C}}$	$Z-\underset{C}{\overset{\|}{C}}$	$Z-\underset{NH}{\overset{\|}{C}}$	$Z-\underset{O}{\overset{\|}{C}}$	$Z-\underset{S}{\overset{\|}{C}}$	Compound to be attacked
$-C\cdot$						sulfur
		$\phi_3\equiv C-Cl$ (P)				rubber
$-O\cdot$	RONO (AS) / R₂NCl (AS)			$\left(\phi-C(=O)-O-\right)_2$ (VA)		sulfur
	ROOH (C) / ROOR (C)	ϕOH (AO)		$\left(\phi-C(=O)-O-\right)_2$ (C)		rubber
$-S\cdot$	RSNO (AS) / RSCl (AS)	ϕSCl (AS); $\phi-N=N-S-\phi$ $\rightarrow \phi\cdot + N_2 + \cdot S-\phi$ (VA)	$RC(=NH)-SH$ (VP); benzothiazole-2-thiol (VA)	$(\phi-C(=O)-S-)_2$ (VA)	$R_2N-C(=S)-SH$ (VA); $(R_2N-C(=S)-S-)_2$ (VA)	sulfur
		$\phi-N=N-S-\phi$ (P)(C); $\phi-SH$ (P)	benzothiazole-2-thiol (P)	$\phi-C(=O)-SH$ (P); $(\phi-C(=O)-S-)_2$ (C)	$(R_2N-C(=S)-S-)_2$ (C)	rubber
$-N\cdot$	$R_3\overset{+}{N}R'\;\;Cl^-$ (VA)	$\phi-NH_2$ (A); $\phi-\underset{NO}{N}-\phi$ (AS)	trichloromelamine structure (AS); $\underset{\phi-NH}{\overset{\phi-NH}{\diagdown}}C=NH$ (VA)	trichloroisocyanuric acid structure (AS); N-chlorosuccinimide structure (AS)	$CH_3-NH-C(=S)-NH_2$ (VP); $CH_3-S-C(=S)-NH_2$ (VP)	sulfur
	$R_3\overset{+}{N}-\phi\;\;Cl^-$ (P)	$\phi-NH-\phi$ (AO)				rubber

or nitroso-compounds of imide, imine, alcohol, mercaptan or other S- and O-derivatives were found to have such characteristics.   Accelerators for vulcanization such as quarternary salts and disulfides involve components with moderate radical affinity for the sulfur molecule.

As illustrated in Table VII, rubber chemicals including commercial ones can be classified, into groups which have structual units such as $Z-\overset{\parallel}{\underset{Y}{C}}-X\cdot$, where both X and Y represent C, N, O or S.   The modes of action of reagents and the relation between polarity and stability are well interpreted in Table VII.

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