trol is required to prevent excessive heat build-up and decomposition of the polyvinyl chloride. This can be accomplished by starting the blow at lower temperatures, followed by an increase in heat if necessary. Heating cycles are also important. When the product is held at elevated temperatures for extended periods, either in the mold or during the final expansion, the gas bubbles coalesce and form larger cells. Thus, each recipe will require some experimentation to achieve the optimal balance of cell structure, final volume, and rate of blow.

A number of other polymers have also been blown satisfactorily using p,p'-oxybis-(benzenesulfonyl hydrazide). Included are Butyl rubber, neoprene, GR-S, high reclaim stocks, and various rubber-resin blends. Each of the polymers required a particular set of curing or processing conditions for optimum blow. These conditions, however, appeared to be characteristic of the polymer and were not influenced appreciably by the presence of the blowing agent. Thus, it appears that p,p'-oxybis-(benzenesulfonyl hydrazide) can find application in the production of a wide variety of expanded, cellular products.

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By-Products of the Thiophene Synthesis

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The production of thiophene from *n*-butane and sulfur has been described by Rasmussen, Hansford, Sachanen, Myers, and Ray (5, 15, 16). The yield of thiophene is about 40% and an equal percentage of a black mobile liquid by-product is formed, which boils above 170° C. at atmospheric pressure and has been classified as thiophene tar. The general properties of this byproduct have been described by the same authors (6). The present article deals with the composition of this tar and with the two compounds which comprise the bulk of its lower boiling components.

THIOPHENE TAR REFINING

The composition and physical properties of thiophene tar vary when it is kept in storage. In Table I it is shown that the tar, whether refined immediately (fresh tar) or after six months of storage (aged tar), is singularly devoid of free sulfur and hydrogen sulfide and has a constant amount of benzene-insoluble sludge and high molecular weight components. However, the composition of the lower molecular weight portion, usually less than 45% of the total tar, changes considerably during storage.

The lower molecular weight constituents can be isolated from the tar in several ways.

DESTRUCTIVE DISTILLATION. When an aged tar (6 months in storage) is distilled under a vacuum of 1 to 5 mm. of mercury, a 40 to 45% yield of distillate is obtained over a pot temperature range of 80° to 160° C. Above this temperature extensive and uncontrollable decomposition takes place. Redistillation of the

distillate at 2 mm. pressure through a column packed with glass helices resolves it into two major components. One component, comprising 30% of the original tar, boils at 40° to 45° C. and the other, comprising 15%, boils at 120° to 125° C. The former has been identified as 3-thiophenethiol. The latter has been classified tentatively as thiolanedithione on the basis of preliminary data concerning its physical and chemical properties.

SOLVENT EXTRACTION. By the use of acetonitrile in a typical 3-stage extraction, an aged tar can be resolved into two equal parts of considerably different molecular weight.

Fraction	Yield.	Molecular	Sulfur,
	Weight %	Weight	Weight %
Extract Raffinate Charge (aged tar)	52 48	170 350 280	57.6 55.1 56.3

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Components	Fresh Tar, % by Weight	Aged Tar % by Weight
3-Thiophenethiol	20-30	< 5
3-Thiophenethiol derivative ^a	< 5	20-30
Thiolanedithione	10-20	10-20
Free sulfur and hydrogen sulfide	<1	<1
Benzene-insoluble sludge	5-10	5-10
High molecular weight tars, molecular weight	t	
>350, average composition ^b (C ₄ H ₄ S ₂) _n	40-50	40-50
Aged product from which 3-thiophenethic	ol can be regene	erated.

* Aged product from which 3-thiophenethiol can be regenerated b Sulfur calculated for $(C_4H_4S_2)_n$, 55.2%; sulfur found, 55.0%. Distillation of the extract under 2 mm. pressure results in a 60 to 65% yield of distillate from which the same two cuts described above can be isolated. The yield, based on the original charge, of 3-thiophenethiol and thiolanedithione is 10 and 20%, respectively. Apparently, a considerable portion of the material which could be converted to 3-thiophenethiol by destructive distillation is lost in the raffinate.

STEAM DISTILLATION. By passing steam through a freshly made tar, a 25% yield of 3-thiophenethiol can be realized. Less than 5% can be recovered in this manner from an aged tar. Vacuum distillation at moderate temperatures effects the same results.

When aqueous hydrochloric acid and zinc dust are added to these steam treated tars and the introduction of steam continued, a 20 to 30% yield of 3-thiophenethiol is obtained from the aged tar and less than 5% from the fresh tar.

The instability of the 3-thiophenethiol appears to be responsible for the change in the composition of the tar upon aging. Although the product of this transformation is unknown, it is obvious that it will revert to the original 3-thiophenethiol upon destructive distillation or treatment with hydrochloric acid and zinc dust. Therefore, the over-all yield of 3-thiophenethiol which can be obtained by this process is not affected by the instability of 3-thiophenethiol and can amount to about 1 pound for every 4 to 5 pounds of thiophene.

IDENTIFICATION AND PROPERTIES OF 3-THIOPHENETHIOL

The principal product obtained by destructive distillation of aged thiophene tar or by steam distillation of fresh tar is an almost colorless liquid of offensive odor, which boils at 171° C. at atmospheric pressure or at 40° to 45° under 2 mm. pressure. It is miscible at 35° C. with diethyl ether, acetone, benzene, *n*heptane, acetonitrile, and stoichiometric amounts of 30% sodium hydroxide solution. It is immiscible with ethylene glycol and glycerol and its solubility in water is less than 0.05% by weight at 25° C. There is a marked intensification of color and increase in refractive index of this material upon storage, regardless of the presence of the more familiar inhibitors or the absence of air and light. However, the pure material can be recovered almost quantitatively by vacuum distillation.

This material undergoes chemical reactions which are characteristic of the thiol group (3). Its reaction with sodium hydroxide and acetic anhydride to form a stable thioacetic ester from which the original product can be recovered in semiquantitative yields by saponification followed by steam or vacuum distillation, has been recommended as a method of handling it in large quantities.

Infrared analysis of this compound confirms the presence of a thiol group and of a thiophene ring. These data in conjunction with the properties shown in Table II indicate that the compound has one of the two isomeric structures, 2-thiophenethiol (I) or 3-thiophenethiol (II).



Both isomers have been synthesized. The infrared absorption spectra of these compounds and derivatives are compared with those of the tar component in Figure 1.

2-Thiophenethiol was prepared from 2-iodothiophene (III) (11, 12). To 2.5 grams (0.1 mole) of magnesium turnings (for Grignard reactions, Eastman) in 50 ml. of anhydrous ether was added with stirring a solution of 20 grams (0.1 mole) of 2-iodothiophene in 50 ml. of ether, at a rate sufficient to maintain a good rate of ether reflux. No difficulty was encountered in initiating the reaction. To the Grignard derivative (IV) thus

TABLE II.	COMPOSITION AND	PROPERTIES C	OF THIOPHENETHIOL
	FROM TH	IOPHENE TAR	

Property	Product from Tars	Theoretical for (C4H3S)SH
Specific gravity at 25 ^b C. Refractive index, n ² 0 Boiling point, ° C. Carbon, weight % Hydrogen, weight % Sulfur, weight % Mercaptan sulfur, weight % Saponification number Metralization number Molecular weight Sulfur, weight % of mercury derivative ^a Sulfur, weight % of 2,4-dinitrophenyl sulfide ^a Melting point, 148-149° C.	1.251 1.6201 1.1 at 760 mm. 41.9 3.5 54.9 28.0 438 442 128 29.6 22.4	41.3 3.45 55.2 27.6 483 483 116 29.7 22.7

formed was added slowly 3.1 grams (0.1 mole) of sulfur (sublimed, Merck). After refluxing for 1 hour the product was poured quickly into a dilute hydrochloric acid solution. The thiophenethiol was isolated by steam distillation and a conversion of 20 to 30% based on 2-iodothiophene obtained. The yield could probably be increased by reduction of the polysulfides formed in the process with zinc dust and hydrochloric acid.







Figure 1. Comparison of Infrared Absorption Spectra of Thiophenethiols Cell length, 9.0074 = 0.0002 cm.

3-Thiophenethiol (II) was prepared from 3-iodothiophene (14, 17, 21) in a similar manner. To 2.6 grams (0.1 mole) of magnesium turnings in 50 ml. of anhydrous ether was added with stirring a solution of 1 gram of methyl iodide and 24 grams (0.1 mole) of 3-iodothiophene in 50 ml. of ether. The reaction mixture was warmed for 1 hour after all evidence of reaction had ceased and 3.5 grams (0.1 mole) of sulfur were added slowly. The product was poured into a dilute hydrochloric acid solution and the 3-thiophenethiol removed from the mixture by steam distillation. It was separated from unreacted 3-iodothiophene by dissolving it in a dilute base under an atmosphere of nitrogen, removing the 3-iodothiophene by ether extraction and reacidification.

tion. A yield of 21% based on reacted 3-iodothiophene was obtained.

The formation of this Grignard compound was more difficult to initiate than that of the 2-derivative and since half of the 3iodothiophene was recovered unchanged it is probable that a mole equivalent of methyl iodide should have been used in order to ensure a more complete formation of the Grignard derivative (18). This was not done at the time since it was feared that the use of large amounts of methyl iodide would complicate the subsequent reaction with sulfur.

The position of the iodine on the nucleus was confirmed by the reaction of the thienylmagnesium iodide with carbon dioxide to give 3-thiophenecarboxylic acid with an observed melting point of 137° C.; the reported melting point (20) is 137° to 138° C.

The two synthetic thiophenethiols and the product obtained from the tar give crystalline derivatives with 2,4-dinitrochlorobenzene (2), and a comparison of their melting and mixed melting points shows the tar by-product to be 3-thiophenethiol.

2,4-Dinitrophenyl Sulfide of	Melting Point, ° C
2-Thiophenethiol	119 -119.5
3-Thiophenethiol	132.5-133
Thiophenethiol from tar	133 -133.5
3-Thiophenethiol and tar thiol	132.5-133

This is confirmed by the close similarity in infrared absorption spectra of 3-thiophenethiol and the tar product, and their marked difference from the spectrum of 2-thiophenethiol, which is given in Figure 1.

PROPERTIES AND TENTATIVE CLASSIFICATION OF THE C4H4S, BY-PRODUCT

The second product, isolated from fresh or aged tars by vacuum distillation or solvent extraction, is a deep red liquid of unpleasant odor, which boils at 120° to 125° at 2 mm. pressure. Its composition corresponds to the formula, $C_4H_4S_8$.

The respective calculated and found results of analyses on this compound were for carbon, 32.4 and 33.9%; for hydrogen, 2.7 and 2.7%; for sulfur, 64.8 and 63.3%; and for molecular weight, 148 and 157. Infrared absorption studies show that no thiophene ring or thiol group is present. The absence of the latter is substantiated by a negative response to alcoholic silver nitrate.

This compound dissolves slowly in aqueous potassium hydroxide. In hot alcoholic potassium hydroxide it reacts with two mole equivalents of the base and undergoes a color change from red to purple. Acidification of this solution results in the evolution of approximately 1 mole equivalent of hydrogen sulfide. dipped into a mild oxidizing solution. Then a fast khaki color was obtained.

Destructive hydrogenation of this compound with Raney nickel according to the procedure of Mozingo (13) yields *n*-butane as the major product.

Of the several types of structures that could be drawn from the formula, $C_4H_4S_3$, a thiolanedithione (V) would have properties most similar to those shown above. Moreover, it is the most logical structure by analogy to the other products of the reaction, since it can be considered to be a tautomeric form of thiophene-dithiol (VI).

An ultraviolet absorption spectrogram of this material shows strong specific extinction coefficients at wave lengths of 230, 250, 335, 415 m μ , and substantial absorption beyond 500 m μ . Since compounds containing conjugate systems, such as diacetyl (θ), absorb much longer wave lengths than similar compounds of nonconjugate structure, such as acetylacetone and acetic anhydride (1), and since compounds containing a C—S group tend to absorb similar though somewhat longer wave lengths than their C—O containing analogs (10), the 3,4- and 2,3-thiolanedithiones (VII and VIII), which contain conjugate systems, are preferred to their 2,4- and 2,5-isomers.



Further speculation as to the exact structure must await the isolation of this material in greater purity than has been obtained thus far.

FORMATION OF 3-THIOPHENETHIOL AND THIOLANEDITHIONE

On the basis of experimental evidence it appears that thiophene, 3-thiophenethiol, and the speculative thiolanedithione are primary products of the reaction of butane with sulfur at elevated temperatures. For the purpose of simplification in outlining a mechanism for the formation of these compounds, it is



The presence of a reducing agent, such as zinc or sodium hydrogen sulfite, hastens the formation of the purple solution; this reaction can be reversed by introducing a mild oxidizing agent. Moreover the color disappears completely upon further reduction at 100° C.

An effort was made to dye wool cloth with the purple solution but the color quickly faded unless the dyed cloth was immediately Figure 2. Possible Mechanism of Reactions Leading to Thiophene and Its Tar Derivative



convenient to consider butadiene to be the principal hydrocarbon reactant (3, 8), although the same conclusions can be reached with butenes. Assuming then that substitution of the hydrogen atoms in butadiene by sulfur is stepwise and rate determining, and that at high temperatures all six hydrogens are substituted at approximately equal rates (4), a possible mechanism can be formulated as shown in Figure 2.

It is assumed, too, that formation of a 5-membered ring is the most likely cyclization reaction and that two sulfur atoms will not remain on one carbon atom during ring closure. These assumptions are based on the absence of 2-thiophenethiol and 6-membered rings containing a disulfide linkage. Moreover, substitution of hydrogen atoms on the thiophene ring by sulfur is thermodynamically unfavorable and all attempts to bring this about under the conditions of the reaction have failed. The mechanism, therefore, conforms with the experimental data on thiophene and thiophenethiol and lends support to the selection of a 3,4-isomer of thiolanedithione.

Furthermore, an estimation of the product distribution can be made, assuming random substitution of the hydrogen atoms of butadiene by sulfur. In order to form thiophene it is necessary for sulfur to attack the hydrogens on carbon atoms 1 or 4 (total hydrogens equal four) as shown in Figure 2. Thiophenethiol formation requires an initial attack at carbons 2 or 3 (total hydrogens equal two). This probability indicates a mole ratio of the precursors of thiophene and thiophenethiol of 2 to 1.

In order to form thiophenethiol, it is necessary for sulfur to attack the hydrogens on carbon atoms 1 or 4 (total hydrogens equal four) of the intermediate (IX). The formation of 3,4thiolanedithione requires substitution of the hydrogen atom at carbon 3. Hence, the probable mole ratio of the precursors of 3-thiophenethiol and 3,4-thiolanedithione is 4 to 1 and the overall mole ratio of these three major products is 10 to 4 to 1 (4).

	Calculated		Actual
Compound	Mole %	Weight %	Weight %
Thiophene 3-Thiophenethiol 3,4-Thiolanedithione	66.7 26.7 6.6	58 32 10	67 23 10

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Oxidation of Unvulcanized Cold Rubber

INFLUENCE OF ADSORPTION BY CARBON BLACK

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ARBON black gel (7), the benzene-insoluble carbon-rubber Complex developed in unvulcanized mill-mixed tread compounds, to which has been ascribed a fundamental role in the reinforcement of rubber, usually contains 30% or more of insolubilized rubber associated with the carbon, the exact percentage depending on the polymer, the carbon, and the mixing conditions employed. The development of this carbon gel complex, of which a typical example is shown in the electron photomicrograph in Figure 1 (3), results from a combination of factors during the mixing stage, including the adsorptive activity of the carbon, the oxidative reactions on the polymer and the mechanical shearing of the polymer. To date no satisfactory approach had been found for following the progressive growth of this carbon gel complex, as a means for assessing the role played by these various factors, and

for determining the mechanism whereby this high percentage of insolubilized rubber is developed.

Attempts to approach this level of insolubilized rubber by dilute adsorption tests have failed, with values in the range of 1 to 3% by weight on carbon invariably resulting (7). This level is much lower than that found in the carbon gel complex of millmixed compounds, as shown in Figure 2. This range of values has not been altered significantly by varying such factors as the type of polymer, the grade of carbon, the solvent, the ratio of carbon to rubber, the temperature, or the tumbling time (2, 7). Adsorption from dilute solution therefore appears inadequate as a method for following the progressive development of the carbon gel complex, through failure to bridge this gap between 3 and 30%insolubilized rubber.