# Reactions of Alkyl Pyridines with Air and Ammonia in the Vapor Phase

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XIDATION of alkyl pyridines can lead to the production of niacin, an important vitamin of the B-complex. Almost 1,500,000 pounds of niacin and niacinamide were produced in 1950 (9). Numerous liquid phase processes, requiring the use of oxidizing agents, such as potassium permanganate (1), sulfuric acid (11), or nitric acid (10), have been devised for the production of the vitamin. Potentially, air used in conjunction with a catalyst should be the most economical of oxidizing agents and, indeed, air oxidation of the alkyl pyridines in the vapor phase has been reported (2, 5, 7), but these investigations have been characterized by low yields. Porter, Erchak, and Cosby (8) carried out the oxidation in the presence of ammonia and isolated cyanopyridines. In the course of the present studies it was found that increased yields were obtained when the oxidation was performed in the presence of ammonia, and that the reaction products were cyanopyridines and pyridine carboxamides. The studies were concerned with the catalytic interaction of alkyl pyridines in the vapor phase with air alone, with ammonia alone, and with both air and ammonia. Other amines were also used in place of ammonia. No attempts were made to determine optimum conditions leading to maximum yields, as

this study was exploratory in nature and was intended, primarily, to indicate the usefulness of the apparatus and to identify the products formed.

# APPARATUS

The component parts of the apparatus are illustrated in Figure 1. Air at 50 pounds per square inch gage from a reciprocating compressor, A, was dried and filtered in a Drierite cylinder, B, which consisted of a 4-inch standard pipe, 2 feet long, three quarters filled with 6- to 8-mesh Drierite, and the remainder packed with glass wool. The air pressure was reduced to 5 pounds per squareinch gage through two 1/4-inch pressure reducing values, C. A surge tank, D, 12 inches in diameter and 18 inches long, in the air line was used to dampen any sudden pressure fluctuations. The air stream, controlled by 1/8-inch brass needle valves, was divided into primary air, E, and secondary air, F. Both primary and secondary air were measured

 $\bigcirc$ F SECONDARY AIR HTR. E) PRIMARY AIR REACTOR AMMONIA Η.  $\bigcirc$ G ROTAMETERS VAPORIZER AMMONIA (K) CYLINDER D EXIT COND. SURGE TANK (C) Ń  $\bigcirc$ AIR SUPPLY 50 PSIG DRIERITE Þ B (A)CYLINDER PRODUCT RECEIVER Figure 1. Diagram of Apparatus 1630

through rotameters, G, having a maximum capacity of 2 liters per minute of air, calibrated at 70° F. and atmospheric pressure. The ammonia flow, controlled by a  $^{1}/_{8}$ -inch alloy steel needle valve, was metered through rotameters, G, which were capable of measuring 0 to 1 liter per minute or 0 to 70 cc. per minute. The primary air and ammonia were mixed and sparged through the vaporizer flask, H, which contained the alkyl pyridine.

The secondary air was introduced into the vapor stream prior to entering the reactor. The vaporizer, H, was a 125-ml. threenecked pear-shaped borosilicate glass flask which was immersed in an oil bath. The vaporizer bath was heated by a 200-watt immersion heater and controlled automatically so as to maintain a constant temperature in the vaporizer. Temperatures were read from thermometers placed in the vaporizer and bath. The vapor stream was conducted through an electrically heated and insulated pipe, I, to the reactor, J. The vertical tube reactor was built of stainless steel Type 304 pipe, 1 inch in diameter and 10 inches long, to which was welded a jacket made of a 3-inch steel pipe, 8 inches long, opened at the top.

The jacket was filled with a eutectic mixture of salts consisting

of lithium, sodium, and potassium nitrates (27.3, 18.3, and 54.4%, respectively) with a eutectic point at 120° C. A 1000-watt stainless steel immersion heater was used to heat the salt bath. The top of the reactor was provided with a 1-inch pipe tee (stainless steel Type 304), which served as an inlet for the vapor stream and also as a port for inserting the thermowell  $(1/_4$ -inch stainless steel Type 304), for charging the catalyst and glass beads and for closing the system. The stuffing box at the top of the reactor consisted of two bushings made from stainless steel Type 304 plugs. One bushing was made from a 1-inch plug. This had a drilled hole 5/16 inch in diameter. The other bushing was made from a  $1^{1/4}$ -inch plug. This had a 1-inch thread from the top down on the inside halfway through the plug; the remainder had a drilled hole 5/16 inch in diameter. The bottom of the reactor tube was provided with a reset to support the screen.

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Thermocouples were used to measure temperatures within the reactor and the salt bath. A powerstat was used to control the input to the immersion heaters; temperatures were controlled manually.

The collecting system for the products of the reaction consisted of steel exit condenser, K, 6 inches long coupled to the reactor, a product receiver, L, two Friedrick's condensers, M, TABLE I. CATALYTIC INTERACTION OF ALKYL PYRIDINES WITH AIR IN THE VAPOR PHASE

Alkyl Pyridine	Cataly Vol., Cc.	st <u>Tem</u> Vapo- rizer	Reactor bath	° C. Cata- lyst	Air L./Hr.	Alkyl Pyridine, G./Hr.	Dura- tion of Run, Hr.	Products Isolated and Yield
β-Picoline <sup>4</sup> 3-Ethylpyridine Aldehyde collidine 3-Acetylpyridine	20 20 20 20	50 50 55 125	300 320 280 320	300 335 280 325	30 30 30 30	$2.5 \\ 4.6 \\ 1.2 \\ 2.8$	$5.9 \\ 4.0 \\ 6.0 \\ 2.3$	Niacin, 17% Niacin, 1% Niacin, 1%; nico- Niacin, 1%; nico-
2-Methyl-5-acetylpyridine 3(α-Aminoethyl)pyridine 2-Methyl-5(α-aminoethyl) pyridin	20 20 e 20	$110 \\ 110 \\ 110 \\ 110$	280 350 350	300 380 380	30 30 30	$egin{array}{c} 1.7\\ 4.2\\ 2.4 \end{array}$	$\begin{array}{c} 5.3\\ 1.5\\ 4.5\end{array}$	Niacin, 2% Nicotinonitrile, 1% Nicotinonitrile, 7%
<sup>a</sup> A ferric vanadate catalyst was	Harshaw	vanadiu	m was u	used in al	l other exp	eriment	s.	

one Allihn condenser, N, a solids separator, O, and a bubbler, P, as shown in Figure 1. Tap water was used for cooling.

# PROCEDURE

To charge the reactor a flexible stainless steel screen was inserted at the bottom of the reactor tube on the reset provided for it. The thermocouple well, supported by the screen, was inserted and centered and a measured volume of catalyst was poured evenly around the well. Glass beads (15 cc.) were added over the catalyst bed to provide a preheat zone. The system was closed with the stuffing box arrangement with asbestos packing around the well. After charging the unit with catalyst, the vaporizer and vapor line between the vaporizer and reactor were heated to operating temperature. The salt bath was heated carefully, making allowance for the temperature rise caused by the exothermic reaction. Vaporizer temperatures were calculated to provide mixtures which contained a 400 to 1000% excess of oxygen beyond that theoretically necessary to produce the pyridine carboxylic acid. With the vaporizer, vapor line, and salt bath at the proper temperatures, the required amount of air and ammonia were mixed and sparged through the alkyl pyridine contained in the vaporizer. The weight of alkyl pyridine consumed was determined by difference, weighing the vaporizer and contents before and after a run. At the completion of a run, the system was blown out (purged) with air for 10 minutes using the secondary air line.

### CATALYST

Commercial and laboratory prepared catalysts were investigated in this study. The commercial catalysts were Harshaw brand, designated as Harshaw vanadium (V-X-L-231-17-T<sup>-1</sup>/<sub>8</sub>), copper chromite (Cu-X-1205-10-T<sup>-1</sup>/<sub>8</sub>), and molybdenum (Mo-0601 T  $^{1}/_{8}$ ). Other commercial catalysts were Alcoa alumina, Universal Oil Products dehydrogenation and dehydrogenation catalysts (Type J-2), and Davidson vanadium on silica (2202 S).

A ferric vanadate catalyst was prepared according to the method of Maxted  $(\theta)$  by adding an aqueous solution of 1 mole of ferric nitrate to an aqueous solution of 3 moles of ammonium metavanadate. The resulting brown precipitate was filtered off, washed thoroughly, and dried at 100° to 110° C. The dried lumps were ground to 4- to 10-mesh size particles, and heated to 400° C. Two pumice-supported catalysts were prepared as the oxide of the metal as described by Houghton and Lowdermilk (4). Nickel and iron oxides were prepared by impregnating pumice (6- to 8-mesh), which had been cleaned by boiling in dilute nitric acid, in the molten nitrate. The impregnated pumice was then dumped on a stainless steel screen and allowed to drain. The nitrate was decomposed in a tube at 300° to 400° C. in a stream of air for 2 hours. Alumina-supported catalysts were also prepared by the same technique on activated alumina chips (6- to 8-mesh). The metals used included chromium, iron, cobalt, silver, cerium, tin, platinum, lanthanum, and bismuth. A vanadium catalyst was prepared by impregnating

1/s-inch pellets of Harshaw alumina (Al-0104) in 5% ammonium vanadate solution; the pellets were thoroughly washed, dried, and heated to 400° C. for 6 hours in a stream of air. Tungsten oxide, magnesium dioxide, and metallic copper were also tried

A brief, orientational search was made to determine which catalysts best promoted the conversion of  $\beta$ -picoline to nicotinonitrile. This search was by no means thorough, and in most cases only one run was made with each catalyst. It was found, in general, that elements of the V, VI, and VIII groups of the periodic table yielded nicotinonitrile whereas other metals did not. The Harshaw vanadium gave a 60% yield, ferric vanadate and the chromium on alumina each gave 13% yields. The Harshaw molybdenum, Universal's hydrogenation and dehydrogenation catalysts, iron on alumina, and nickel on pumice, each gave 1% yields, while all other catalysts gave negative results.

#### **REACTIONS OF ALKYL PYRIDINES**

REACTION WITH AIR. Various alkyl pyridines were permitted to react with atmospheric oxygen over a vanadium catalyst (Table I). In each case hydrogen cyanide, carbon dioxide, and water were identified among the reaction products together with low yields of niacin. The highest yield, 17%, was obtained from  $\beta$ -picoline. Aldehyde collidine (2-methyl-5-ethylpyridine) gave a poor yield of niacin, and isocinchomeronic acid could not be isolated. Presumably, the dicarboxylic acid was decarboxylated to niacin.

$$_{H_{3}C}\left(\bigcap_{N}^{C_{2}H_{\delta}}\rightarrow\left[H_{0OC}\left(\bigcap_{N}^{COOH}\right]\rightarrow\left(\bigcap_{N}^{COOH}\right)\right]$$

Since nicotine has been converted to nicotinonitrile (3, 12), it was suggested by Duesel that nitrogen in the side chain of an alkyl pyridine might give rise to the corresponding cyanopyridine. In consequence of this reasoning, it was found that 3-pyridylethylamine and 2-methylpyridine-5-ethylamine both yielded nicotinonitrile.



As would be expected 3-acetylpyridine yielded niacin, but surprisingly, some nicotinonitrile was also identified. Apparently, an oxidation product such as hydrogen cyanide took part in the reaction to form nicotinonitrile.

REACTION WITH AMMONIA. Attempts to obtain nicotinonitrile from  $\beta$ -picoline and ammonia without air failed at temperatures below 350° C. At a temperature of 570° C, and using the Harshaw vanadium catalyst, nicotinonitrile was obtained in trace amounts, but much of the  $\beta$ -picoline was recovered unchanged.

		_				Flow Ra	ates		
Alkyl Pyridine	Cat. Vol., Cc.	Tem <u>r</u> Vapo- rizer	Reactor bath	Cata- lyst	Air, l./hr,	Am- monia, l./hr.	Alkyl pyridine, g./hr,	Time of Run, Hr.	Products Isolated and Yield
α-Picoline β-Picoline 3-Ethylpyridine 4-Ethylpyridine 2,6-Lutidine	20 20 20 40 40 20	48     40     48     40     4	300 310 305 320 310 305	305 325 310 370 360 305	21 30 21 60 60 21	$23\\34\\25\\4\\25$	$\begin{array}{c} 4.0\\ 2.1\\ 2.4\\ 2.2\\ 2.0\\ 1.1 \end{array}$	$3.0 \\ 5.25 \\ 2.1 \\ 5.0 \\ 2.8 \\ 2.3 $	α-Picolinamide, 5% Nicotinonitrile, 60% Isonicotinonitrile, 23% Nicotinonitrile, 47% 2-Cyanopyridine-6-car- boxamide and 2- cyano - 6 - methyl- pyridine, 1%
Aldehyde collidine <sup>a</sup>	40	45	320	350	60	4	1.5	5.5	Nicotinonitrile, 37.5%; 6-cyanonicotinamide, trace
Aldehyde collidine	20	60	290	295	<b>21</b>	11	0.9	2.8	6-Cyanonicotinamide,
3-Acetylpyridine 2-Methyl-5-acetyl- pyridine	20 20	90 110	$\frac{290}{325}$	$\begin{array}{c} 350\\ 350\end{array}$	36 30	$^{11}_{5}$	1.1 1.6	$3.2 \\ 5.8$	Nicotinonitrile, 10% Nicotinonitrile, 11%; 6- cyanonicotinamide, 07%
Quinoline 2,4,6-Collidine 4-n-Amylpyridine	$20 \\ 20 \\ 20 \\ 20$	$90 \\ 59 \\ 44$	300 300 300	$305 \\ 310 \\ 310 \\ 310$	$\begin{array}{c} 25\\21\\21\end{array}$	$28 \\ 25 \\ 25$	$\begin{array}{c} 0.8 \\ 1.5 \\ 0.23 \end{array}$	$2.5 \\ 3.0 \\ 2.5$	No identifiable product No identifiable product No identifiable product
<sup>a</sup> A vanadium catalyst on alumina was used; in all other instances the catalyst was Harshaw vanadium.									

TABLE II. REACTIONS OF ALKYL PYRIDINES WITH AIR AND AMMONIA IN THE VAPOR PHASE

REACTION WITH AIR AND AMMONIA. A number of alkylpyridines mixed with air and ammonia were allowed to react over a vanadium catalyst under conditions set forth in Table II, which lists the products isolated and the yields that were obtained. Beta- and gamma-substituted alkyl pyridines yielded the corresponding nitriles, whereas,  $\alpha$ -picoline gave picolinamide. Disubstituted alkyl pyridines gave both cyano and carboxamido derivatives. Aldehyde collidine gave either 6-cyanonicotinamide or nicotinonitrile depending on the temperature.



No identifiable product other than water, carbon dioxide, and hydrogen dioxide could be identified from quinoline, 2,4,6-collidine, or 4-n-amylpyridine.

To identify the end products, each reaction mixture was extracted with ethyl ether. The ether layer was dried with anhydrous sodium sulfate, and the ether was removed in vacuo. Quantitative data were obtained by means of a copper nicotinate method in which 1.5 grams of the ether residue were hydrolyzed with sodium hydroxide (2 grams of sodium hydroxide per 25 ml. of solution) at reflux temperatures for 1 hour. To the reaction mixture, acidified to pH of 6.6 to 6.9, a saturated solution of copper sulfate was added slowly, with stirring, until precipitation was complete. The precipitate was allowed to digest for 3 hours. The copper precipitate was filtered, washed with acctone, and dried at 110° C. The product, crude copper nicotinate, frequently contained small amounts of copper isocinchomeronate, which was separated with 90% formic acid. Copper nicotinate disolved in the formic acid, but the copper isocinchomeronate did not. Yields were calculated from the weights of the copper salts.

Individual products were, in general, separated by fractionation and identified by their physical constants and by comparison with authentic samples; for example, the compound obtained from the oxidation of  $\alpha$ -picoline contained 23.2% nitrogen and melted at 107° to 108° C. Its picrate melted at 170° to 171° C. This product was identical with an authentic sample of picolinamide. Mixed melting points of the amide and picrate with known samples were not depressed.

A product isolated from the oxidation of 2,6-lutidine in 5% yields, and melting at 72° to 74° C., was assumed to be 2-cyano-6-methylpyridine. It analyzed as follows: carbon, 71.1% theoretical, 70.4% found; hydrogen, 5.1% theoretical, 4.7% found; and nitrogen, 23.7% theoretical, 23.5% found. Its structure was established by comparison with an authentic sample synthesized in unequivocal steps from a known sample of 2-amino-6-methylpyridine. The amino group was replaced by a chlorine atom by means of a Sandmeyer reaction and the resultant chloropicoline was converted by means of cuprous cvanide to 2-cvano-6-methylpyridine. The synthetic product was identical with that isolated from the gas phase oxidation mixture.

Oxidation of 2,6-lutidine gave a second product, melting at 184° to 187° C., which was assumed to be 2-cyanopicolinamide. It analyzed as: carbon, 57.0% theoretical,

56.3% found; hydrogen, 3.4% theoretical, 3.2% found; and nitrogen, 28.6% theoretical, 28.6% found. It was characterized as 2-cyanopicolinamide by hydrolysis to the known product, dipicolinic acid, melting at 228° to 230° C. The only other compounds which can give dipicolinic acid on hydrolysis are pyridine-2,6-dicarboxyamide or 2,6-dicyanopyridine, which have melting points of 295° to 297° C., and 123° C., respectively. Both of these possibilities are ruled out on the basis of melting points and analytical data.

One product, melting at  $275^{\circ}$  to  $277^{\circ}$  C. (decomposed), obtained from aldehyde collidine gave on analysis: carbon, 57% theoretical, 56.5% found; hydrogen, 3.3% theoretical, 3.2% found; and nitrogen, 28.6% theoretical, 29.1% found. It was identified as 6-cyanonicotinamide by comparison with an authentic specimen synthesized from 2-chloro-5-nitropyridine in unequivocal steps as follows: The nitro group was reduced and the resultant amino group was replaced, using a Sandmeyer reaction, by a nitrile group. The nitrile was partially hydrolyzed to yield 2-chloro-5-carboxamidopyridine, and this in turn was converted by replacement of the chlorine atom to 2-cyanonicotinamide which melted at  $275^{\circ}$  to  $278^{\circ}$  C. and did not depress the melting point of the unknown sample.

REACTION WITH AIR AND AMINES OTHER THAN AMMONIA. Nicotinonitrile was obtained in 6% yield by passing  $\beta$ -picoline, monomethylamine, and air over 20 cc. of Harshaw vanadium catalyst at 325° C. at a space velocity of 1500 liters per hour with 30 liters per hour of air, 1.5 liters per hour of monomethylamine, and a vaporizer temperature of 50° C. Using diethylamine, a 3% yield of nicotinonitrile was obtained.

# DISCUSSION

Judging from the products isolated, it seems reasonable to suppose that the alkyl pyridines are oxidized in the gas phase, among other things, to the corresponding acids, which with ammonia form the ammonium salts; these, in turn, appear to be dehydrated to yield amides, and as observed in some instances, the ammonium salts may be completely dehydrated to yield the corresponding nitriles. Aldehyde collidine is presumably oxidized to isocinchomeronic acid which apparently undergoes decarboxylation at higher temperatures, and the resulting carboxylic acid is then converted to nicotinonitrile as before. At lower temperatures decarboxylation presumably does not occur and the dicarboxylic acid is apparently then converted to the 6-cyanonicotinamide. With 2,6-lutidine a stepwise oxidation seems to occur. The monocarboxylic acid is evidently converted to 2-methyl-6-cyanopyridine, whereas more complete oxidation yields the dicarboxylic acid which in turn is converted to 2cyanopyridine carboxamide. While such a sequence of events appears to account for the products isolated following the vapor phase oxidation of the alkyl pyridine in the presence of ammonia, a simple sequence for the conversion of the pyridylethylamines in the absence of ammonia to nicotinonitrile appears unlikely.

#### SUMMARY

A compact, efficient apparatus for laboratory scale study of catalytic gas phase oxidations has been described. It has been used to examine the oxidation of alkyl pyridines in the presence and absence of ammonia. Typical products have been isolated and identified.

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# **Ultimate and Actual Tensile Strengths of Latex Films**

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T HAS been shown previously (2) that in order to determine the actual tensile strength of latex films it is necessary to take into account reduction in cross-sectional area which the film undergoes on stretching. When this is done the tensiles calculated are put on the basis of area at break, in contrast to the usual practice of computing ultimate tensiles as the ratio of breaking load to cross-sectional area of the film before elongation. As confirmatory argument for the above point, a study was made (2) of the tensile strengths of raw polymer and gum vulcanizate films prepared from 53 Type III GR-S latices. It was found that ultimate tensile strengths of the two types of films showed no correlation with each other when the calculations were based on the original cross-sectional areas. On the other hand, when cross-sectional areas at break were used, essentially the same tensile strengths were obtained for both raw polymer and vulcanizate films prepared from a given latex.

This paper presents data for a similar study made on 10 GR-S Type V, eight X-370, and 10 natural rubber latex samples. Type V latex consists of approximately 70:30 butadiene-styrene co-

polymer emulsified with rosin and fatty acid soaps, while X-370 latex contains approximately 80:20 copolymer stabilized with a mixture of fatty and rosin soaps and synthetic emulsifier.

# EXPERIMENTAL PROCEDURE

The latex films were cast by the carbon dioxidemoisture technique described before (1). Following the laying down of films of uncompounded standard Type V and X-370 latices, the samples were allowed to set in the molds for several hours, and the films were removed, cut into a number of squares, and the various strips dried at 100° C. for periods of time ranging from 1/2to 2 hours. After this final drying the strips were stored at 50° relative humidity and 70° F. for 1 hour or longer, and then test strips were cut out with a die, marked with 1/2-inch bench

marks, and tested. The highest tensile obtained from any one cast film was taken to be the tensile strength of the sample. With ammonia-stabilized natural latex it was found that additional drying beyond that obtained during casting was not necessary and that the films were ready for testing after removal from the molds and storage.

Gum vulcanizate films were cast from latices compounded according to the same formula as used with Type III latex (2). The technique for casting was the same as for uncompounded films. In this case, after the films were set, the sheets of rubber were stripped from the molds, cut into smaller sections, and vulcanized at 100° C. for  $\frac{1}{2}$  to  $2^{1}/_{2}$  hours in order to obtain an optimum cure. The vulcanized sheets were then cooled for 1 hour or longer in the air-conditioned test room, died out into standard test strips having 1-inch bench marks, and tested on a special Scott tensile machine (2).

The calculation of the actual tensile strength of specimens was discussed in a previous paper (2).

# TABLE I. ULTIMATE AND ACTUAL TENSILES OF UNCOMPOUNDED AND Compounded Type V Latex Films

01-					$T_{c}$			Se
Bampie	$Tu^a$	$E_u b$	$T_c$	$E_{c}d$	$\overline{\overline{T_u}}$	Su <sup>e</sup>	$Sc^{f}$	$\widetilde{S_u}$
361 362 363 364 365 366 367 368 369 370	173 164 173 181 188 193 198 187 203 216	$390 \\ 515 \\ 485 \\ 515 \\ 510 \\ 615 \\ 600 \\ 580 \\ 615 \\ 685$	268 290 281 300 252 335 305 335 320 303	220 210 240 300 220 250 250 250 250 250	$\begin{array}{c} 1.55\\ 1.77\\ 1.63\\ 1.66\\ 1.34\\ 1.74\\ 1.54\\ 1.54\\ 1.58\\ 1.40\\ 1.40\\ \end{array}$	$\begin{array}{r} 845\\ 1000\\ 1010\\ 1110\\ 1145\\ 1375\\ 1380\\ 1270\\ 1450\\ 1680 \end{array}$	860 890 955 1200 790 1170 1010 1180 1120 1105	$\begin{array}{c} 1.02\\ 0.89\\ 0.95\\ 1.08\\ 0.69\\ 0.85\\ 0.74\\ 0.93\\ 0.77\\ 0.66\end{array}$
Averages	188	551	299	244	$1.60 \pm 0.12$	1227	1019	$0.86\pm0.12$
<sup>a</sup> $T_u$ = ultin <sup>b</sup> $E_u$ = elon <sup>c</sup> $T_c$ = ultin <sup>d</sup> $E_c$ = elon; <sup>e</sup> $S_u$ = actu <sup>f</sup> $S_c$ = actu	mate tensi gation of nate tensi gation of al tensile al tensile	le stren uncomp le stren compou strengt	ngth of pounde ngth of inded t h of ur h of cor	uncon d test s compo cest stri compo	apounded film. strip between be unded film. ip between benc ounded film. led film.	nch mar h marks	<b>ks, %.</b> , %.	