THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

SULFUR IN CORRUGATING MEDIUM

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Progress Report One

to

FOURDRINIER KRAFT BOARD INSTITUTE

MASKING OF DIPHENYL ODOR

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THE INSTITUTE OF PAPER CHEMISTRY

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INTRODUCTION

The present study is directed at masking the odor of diphenyl as used in the shipment of oranges. For a more complete discussion of this problem, the reader is referred to Dr. Pearl's memorandum of July 13 to Mr. Strange.

The odor of diphenyl is rather strong and unpleasant to most people. Therefore, the primary aim of masking here is to conceal the diphenyl odor so that the observer is not aware of its presence, or does not consider the resultant odor objectionable. The second aim is to convert the resultant odor to one very similar to that of an orange. An orange with a nonorangelike odor might be viewed with a certain amount of suspicion, even if the odor is pleasant.

The first stage of this investigation was the impregnation of small kraft strips with benzene solutions of diphenyl and masking chemicals. The air-dried strips were then examined for odor by a "jury" and a preliminary sorting of "good and bad" chemicals effected.

The second stage was a mixing of various chemicals into "bouquets" to improve the "good" chemicals found in the first stage. Various fruit odors and oils were tried here, and the cost of the additives was also considered.

A modification of this technique was the storing of the impregnated strip with an orange in a closed jar to provide a mixed odor from the orange and the chemicals. Psychologically, it was probably better for the

jury members to smell an orange under these conditions than just a card.

Finally a pilot-plant scale of testings was tried with wax coatings of the diphenyl and masking chemicals applied to 1 x 1 x 1-ft. and 6 x 8 x 8-inch boxes. The oranges in these boxes were stored at 40 and 73°. The more satisfactory mixtures found in this stage were then sent to the co-operator for more extensive trials.

Wax coatings were also applied to 2 x 2-inch kraft strips for fungicidal tests by the Bacteriology Group. The samples of blendings sent to the co-operator on July 29 under these conditions showed no difference in fungicidal behavior from diphenyl alone. Therefore, it can be assumed that the chemicals added did not affect the action of diphenyl. Tests of a second group of blendings are now in process.

EXPERIMENTAL

PREPARATION OF 1.5 x 2.75-INCH STRIPS

A stock solution (12%) of diphenyl in benzene was used. The dropwise addition of 0.5 cc. of solution to one surface of a 50-lb. kraft strip and subsequent air-drying for 5-15 minutes in the hood deposited 60 mg. of diphenyl on a surface area of 4.125 sq. in., or the equivalent of 4.63 lb. per M sq. ft. The strip was then placed in a covered jar and opened only for odor tests.

The various masking chemicals were added to the benzene solutions with a capillary pipet, one drop being roughly 10 mg. The ratio of chemical

to diphenyl ranged from 1:6 to 1:400. The last dilution was generally too weak to provide any masking effect.

The odor in each jar, assuming very little evaporation, was that of 60 mg. of diphenyl and the added chemical, emanating from one or both sides of the paper strip. Since the benzene solution, when originally added, penetrated partly to the other side of the strip, the odor might be considered as coming from both sides. In later experiments, with the application of a hot wax mixture, the latter solidified almost immediately when brushed on the inside of a kraft box, so that very little penetration into the kraft liner occurred.

Later tests were tried with the kraft strip stored with an orange in a wide-mouth Mason jar. At first, metal airtight lids were used on the jars, but the sweating of the orange produced a musty odor. Consequently, pieces of qualitative filter paper were substituted as covers, giving a porous cover and a much cleaner odor which was more similar to that in a kraft box.

The use of jars containing oranges allowed many tests to be run on small amounts of material. Duplicate and triplicate tests could be made, eliminating the factor that a single orange might produce an off-odor.

For odor tests, each member of a "jury" was allowed to open a jar and smell the contents without seeing the label. Generally, a control jar, containing only diphenyl, was used initially and at intervals throughout the test because some of the masking chemicals provided

a "deadening" effect on the nose of the observer, invalidating subsequent observations. Eugenol especially was very effective in this regard.

In later tests a more careful effort was made to avoid killing or deadening the sense of smell of the jury members. Odor tests were made at 15 to 30-minute intervals. This limited the number of odor tests to 10 to 15 per day but better results were obtained.

The jury was composed of both men and women, the latter being more critical of chemical smells and disliking anything not of a known agreeable "household" nature. Two of the men, A and S, were well-skilled in detecting faint odors and could detect a faint diphenyl odor where the women would not notice it or would report a "chemical" or medicinal odor. Diphenyl was often described as "flyspray." The men were more tolerant of laboratory odors, often considering them pleasant. whereas a person working outside a chemical laboratory would deem them objectionable. Thus, the men, as a group, would often approve of a blend, whereas the women would not. The reverse case occurred when only a very slight trace of diphenyl was present, being noticed more by A and S than by the women. Chemical N, when not too strong, gave an odor very agreeable to the women (especially G) even though it was not too orangelike.

Therefore, the purpose of the tests listed in Table VIII and the following tables was the production of a bouquet containing enough N to satisfy the women jury members and not too much to be discernible to the men members, and also giving a final odor similar to oranges. Several of the best blends given in the final tables will be sent to Mr. Weathers

for further evaluation. Fungicidal tests will also be run on these blends to note the effect of additives on the diphenyl.

TESTING OF COATINGS IN ORANGE-FILLED BOXES

Each box was painted on the four inner side walls (1 foot square or 48 square inches) with a molten wax-diphenyl mixture. The latter was made by adding a molten mixture of 1 part of Parawax and 4 parts of petrolatum to 5 parts of molten diphenyl. Then were added varying volumes of different chemicals to 18-gram portions (or 6 g. for the small boxes) of the second molten mixture. These were most easily added directly from burets; the mixture was stirred thoroughly and set aside. Each mixture, numbered as in the tables, was remelted when needed and the entire contents brushed on the inside of the respective box. The latter was closed and the wax was allowed to solidify for several minutes. Each box was then filled with oranges and tests were made.

EXPERIMENTAL RESULTS

TABLE I

Preliminary tests of various chemicals were made with impregnated cards stored in glass jars. No oranges were used here. The best chemicals--B, A, D, and E--were then selected for further tests.

TABLES II AND III

Chemicals B, A, D, and E were tested in 1 x 1 x 1-ft. kraft boxes filled with oranges. The key to the box numbers is given in Table II. The evaluation of the boxes is shown in Table III. Mixtures 7 to 12 were

selected and samples of these blends sent to Mr. Weathers. The costs of these blends are given in Table IV.

TABLE V

Varying amounts of a new series of chemicals were used on impregnated kraft strips. (The code letters here are a new series and bear no relation to those in the preceding tables. Tables V to XI represent a new series of blends). Blends D, E, and F seemed most effective in binary mixtures with A. It will be noticed that varying the relative amounts of the two components had a decided effect on the resultant odor. These tests were run in glass jars without oranges.

TABLE VI

These binary mixtures were prepared from calculations based on the Crocker-Henderson odor classification system ("Odor Directory," E. C. Crocker and Florence N. Dillon, The American Perfumer, April-May, 1949). An attempt was made to predict resultant odors of mixtures from the odor data given for the individual components. The only ones that were successful contained Chemical J mixed with F, E, or K. Although most of these odors had the characteristics desired in a blended orange odor, the jury agreed that they were not suitable for an orange.

TABLE VII

A series of odor tests was carried out in jars containing impregnated kraft strips and oranges. In this series, metal lids were

used on the jars and several promising samples may have been rejected because of a musty odor from the sweating orange. Blends containing chemicals N, A, and O seemed to be the most promising.

TABLE VIII

These blendings in jars with paper covers gave bouquets with odors approaching that of an orange. Increasing the amount of Chemical A and cutting down the proportion of N and O was beneficial. Chemical O was preferred to G for removing the musty odor inherent in Chemical N.

TABLE IX.

Odor tests were conducted with orange-filled kraft boxes. A series of three blends was used, also diphenyl alone and boxes containing only oranges. Each type was run in triplicate to check the precision of the jury decisions. As shown in the table, the jury could unhesitatingly detect a box containing only oranges. Boxes containing diphenyl alone were picked by the majority of the jury members as bad, but some errors were observed. Of the three types of blendings supplied, the jury preferred NAO 182, although a sweet rather than an orangelike odor was evident.

TABLE X

More work was then done on a smaller scale, starting with formula NAO 182. The best one was 0.2% NO (1-2), 6.2% of A, 0.8% of I, and 0.8% of M.

TABLE XI

Three promising blends were tried in 8-inch boxes filled with oranges. The jury liked them although they seemed a little pungent, with a lime odor.

CONCLUSION

Five of the most promising blends given in Tables IX, X, and XI will be sent to Mr. Weathers for further trial. Fungicidal tests on these blends will also be run by the Bacteriology Group. Meanwhile, more improvements of the selected blends will be tried, with evaporation tests to note whether or not the masking chemicals evaporate at a more rapid rate than the diphenyl. It is conceivable that the initial odor is pleasing but the final one unpleasant.

THE INSTITUTE OF PAPER CHEMISTRY

John W. Green, Research Associate

R. C. McKee, Chief, Container Section

TABLE I

PRELIMINARY TESTS OF PAPER STRIPS TREATED WITH DIPHENYL AND VARIOUS MASKING AGENTS

Compound Added	Amount, %	Odor Ranking ++	-	--	o	Conclusion
D	4	3	2		1	++
	1		2			--
E	16	4				++
	4	3				++
F	16	2				++
	4				3	--
G	16	3		2		-
	4			5		--
H	16	3	1	1		++
	4			3		--
I	16	2	2	1	1	-
	4				5	--
J	16	4		2		++
	4			3		--
K	16	2	3	1		-
	4	1	1			+
L	4				2	--
M	16			6		--
N	16	1		3		--
O	16	2		2		--
P	16			4		--
Q	16	1	1	1	1	--
R	16	1	1	1	1	--
S	16	2	1	2		--
Control (diphenyl alone)				10		--
B	1			2		--
	0.25			2		--
B	4					
A	4	3			1	++
C	4					
	1	5		1	1	++
	0.25		1	4		--
D	4					
A	4	3	1	3		--
D	4					
B	4	3		2		+
D	4					
B	1	3				++
A	1					
C	1					

TABLE I (Continued)

PRELIMINARY TESTS OF PAPER STRIPS TREATED WITH DIPHENYL AND VARIOUS MASKING AGENTS

Compound Added	Amount, %	Odor Ranking ++	-	--	o	Conclusion
90% Sulfur, 10% Diphenyl and B		1	2	3		--
			1	3		--
B+C		1		4		--
B+A		4	1			++
A,B,C		5				++

Note: In this and following tables, ++ is excellent, + fair, - not so good, and = bad. In the evaluation by the men, + might mean that the diphenyl was masked but the odor was not too good, whereas a + by a woman meant that the resultant odor was good.

TABLE II

KEY TO BOXES OF ORANGES WITH VARIOUS BLENDINGS.
ADDED TO DIPHENYL

Number	B	A	D	E
1 (13)	- - - - blank with no diphenyl at all - - - -			
2	00	00	00	00
3	25	25	00	00
4	25	25	25	00
5	75	25	25	00
6	25	25	00	25
7	75	25	00	25
8	50	00	50	00
9	75	00	50	00
10	50	00	00	50
11	75	00	00	50
12	00	00	00	75

Numbers represent 0.01 of a cc. added to mixture of 9 g. diphenyl, 1.8 g. Parawax, and 7.2 g. petrolatum.

TABLE III

TESTING OF ODOR OF ORANGES PACKED WITH DIPHENYL, ETC.

(1) Tested in a Warm Room, after Being Stored 48 hr. at 40°

Box	1	2	3	4	5	6	Conclusion
13 (1)	++	++	++	++	++	++	++
2	--	-	-	-	--	-	--
3	+	+	-	+	--	+	-
4	+	+	+	++	--	+	+
5	+	+	+	++	--	--	+
6	-	-	-	-	++	--	--
7	-	-	++	++ s	++	++	++
8	+	+	++ o	++	--	--	+
9	--	?	+	++	++	?	--
10	++	?	++ s	++ s	++	++	++
11	++	?	++ s	++	--	++ x	++
12	?	?	++ s	++ s	--	++ p	+

(2) Same, after 48 More Hours Storage at 73°

Box	1	2	3	4(7-26)	Conclusion
13 (1)	++	++ o	++	++ o	++
2	++	-- s	--	-- s	--
3	+ s	++	-	--	-
4	-	++	-	--	--
5	++	-	+	--	-
6	++	++	-	+ s	++
7	++	++	-	--	+
8	++	++	--	--	-
9	+ s	--	-	++	-
10	-	++	--	++ e	-
11	-- s	+ x	-	++	+
12	--	++	-	++ o,s	+

(3) Same, after Storage at 73° for 72 Hours

Box	1	2	3	4	5	6	7	8	9	Conclusion
13 (1)	++	++		++ o	++	++ o	++	++	++ o	++
2	--	--		--	--	++	--	--	-- s	--
3	--	--	+	--	+	++	++	--	--	-
4	--	--		--	-	++	+	--	-	--
5	+	--		--	-	++ s	++	-	-	-
6	+	-	--	--	++	++	--	++	++	-
7	+	--	++	++	++	+	++	++	++	++
8	+	+		--	++	++	++	--	++	+
9	+	++		++	++	+	++	++	++	++
10	+	-		++	++	-	++	++	++ o	+
11	+	-		++ s	++	-	+	++	-	+
12	+	+		++ e	++	--	+	++	++	++

++ excellent odor, + fair, - unsatisfactory, and -- bad. o orange, s safrol and e eugenol. x = bad odor, p = satisfactory odor, both unidentified.

TABLE IV

SAMPLES OF BLENDINGS SENT TO MR. WEATHERS
ON FRIDAY, JULY 29

Amount Chemical	7 cc.	¢	8 cc.	¢	9 cc.	¢	10 cc.	¢	11 cc.	¢	12 cc.	¢
B	90	12	60	8	90	12	60	8	90	12		
A	30	20										
C	30	5					60	10	60	10	90	14
D			60	26	60	26						
Total cost		37		34		38		18		22		14

Note: The above volumes are to be added to 5 pounds of a molten mixture of diphenyl 5, Parawax 1, and petrolatum 4 parts. The costs are based on quotations in the Drug and Oil Reportor, assuming 1 cc. of the above weighs 1 gram.

TABLE V

ODOR TESTS ON IMPREGNATED KRAFT STRIPS IN GLASS JARS

Chemical Added	%	A Added, %	Jury G	A	S	P	R	Conclusion
B	4	0	++	=				=
	2	4	++					
	4	4	+	-				
	2	2	+	-				
	1	2	=	=				Off odor
	1	4	=					
C	4	0	++	+			=	Off odor
	1	2	+					
D	4	0	++	++				
	1	2	-	-		-		Off odor
	1	4		-		+		
	4	4	++	+				Lemon odor
E	4	0	+	+				Off odor
	1	4	++	-	=			Orange odor
	2	2	+	+	=	-		
	2	4	+	+	-	+		
	1	2	=	=	=	=		
	4	4	+	=	=			Bad odor
	1	2		-		-		
F	4	0	+	++				
	2	2	-	+	-			
	1	2	+	=	=	=		
	1	2		++				
	1	4	++	++	+			Orange odor
	2	4		-	-			
	4	4	-	=	=			Bad odor

TABLE VI

ODOR TESTS ON IMPREGNATED KRAFT STRIPS IN GLASS JARS

Chemical	%	Chemical	%	Jury S	Jury P	Jury A	Conclusion
G	2	E	2	=	=	=	=
	2	F	2	=	=	=	=
	2	H	2	=	=	=	Bad odor
	2	I	2	=	-	=	Bad odor
	2	J	2	=	+	=	-
J	2	F	2	+	+	+	+
	2	E	2	+	=	=	+ Lime odor
	2	K	2	=	+	++	+ Lime odor
G	1.3						
and I	1.3	E	1.3	+	+	=	+
G	1.3						
and K	1.3	E	1.3	=	-	-	Bad odor
L	2	E	2	-	+	+	Bad odor
		G	2	=	+	=	-

TABLE VII

ODOR TESTS ON IMPREGNATED KRAFT STRIPS IN GLASS JARS CONTAINING FRUIT

Chemicals Added (based on diphenyl), %					Jury							
M	A	J	H	Total	A	S	P	M	G	I	D	Conclusion
4		4		8	=	=	=	-	=	=	=	Medicinal odor
4	4	4		12	-	-	++	-	=	=	=	" "
4	4		4	12	+	+	+	=	=	=	=	Off odor
4				4	=	=	+	++		-	=	=
4		1		5		=	+		=	=	=	=
4		4		8		=	++	++	-	=	=	Cinnamon odor
4	4	1		9		-	+	++	-	=	=	=

Chemicals Added (numbers give relative amounts, total is 4% in each case)

M	A	J	N									
4	1	1	1		+			++	-	-	=	Bitter odor
4	4	4	1		-		++	+		=	=	
4	0	4	1		++			++	=	=	++	Clean odor
1	1	4	1			=	+		=	=	-	
4		2	2		+	-	+		=	-	=	
2		2	1	(5%)	+	-		++	=		+	Lime or off odor
				(2%)	=	=	+					
1			3					+		=	=	Too much lime odor
4						=	++	++	=	=	-	Off odor

N	A	O	G	Total								
2		1		4	++	-		++	+	+		Sweet, strong but not musty
4		1		4		-		++	++	+		Musty and sweet
2	1			4	+	+		+	=	+		Off odor
1	2	1		4	++	++		++		++		Too sweet
				8				++		++		Too strong
2	2	1		4	++	-		++	++	++		Musty
1	4	1		2	-			+		++		More sweet than orange
				4	-			++		++		More orange than sweet
1	8	1		2			-	+	+			More sweet than orange
				4			-	+	+	+		More orange than sweet
1	8	2		2			+	+		+		
				4			+	+		+		More orange than sweet
2			1	4	-	-		++		=		Musty off odor
4			1	4		-		++	+	=		Flat odor, slightly sweet
2	2		1	2				+	++			Too sweet
				4	+	++			++	++	++	Sweet
2	4		1	4				++	+	+		
1	2		1	4	++	++		++	++	++		Good
				8	++	+		++	++	++		Musty, very sweet
1	4		1	4			-	++	+	+		Orange
1	8		2	4			+		+	+		Orange

TABLE VIII

ODOR TESTS ON IMPREGNATED KRAFT STRIPS IN GLASS JARS CONTAINING FRUIT

Chemical Added	%	Jury W	R	M	I	G	Container Lab.		Conclusion
NAO 141	4			+	+				Sweet and orange
	2			+	++	++			Less orange
NAO 181	4	=		+		+			
	2	=		+		+			More sweet than orange
NAO 182	4	+	++	++	++	++	4+	2=	Orange
	2	+	++	+	+				Sweet and orange
NAG 141	4	-		+	+	+	3+	3=	Sweet
	2	-	-	++		+			
NAG 181	4		=	-	+	+			Orange and sweet
	2		=	-	+	+			Orange and sweet
NAG 182	4	+	++		+	+	4+	2=	Orange
	2			-	=	=			
Blank (diphenyl only)		=	-	=	-	=	5+	1=	
Oranges only							4+	2=	
NAO 182	4		++	+	++	++			

TABLE IX

ODOR TESTS ON DIPHENYL MIXTURES IN 8-INCH BOXES CONTAINING FRUIT

Box	Contents	Time	Jury W	A	B	G	Mi	Ma	D	Conclusion
1	4% NAG 182	9:00	++	=	=	=	=	+		
6		10:40	++			+	++	++		
11		2:40	=	=		=	=	=		
Average			+	=	=	=	=	+		=
2	Diphenyl alone	9:20	++	=	=	=	=	++		
7		11:00	-	+	=	=	=	+		
7		1:00		=			+	-		
12		3:00	-	+				=		
Average			-	-	=	=	=	=		-
3	4% NAO 182	9:40	++	+		++	++	++		
8		11:30	++	=	=	++		++		
13		4:00	+	=		++	++	++		
Average			++	-	=	++	++	++		+ Sweet odor rather than orange
4	Oranges only	10:00		++	++	++	++	++		
9		2:00	++	++	++	++	++	++		
Average			++	++	++	++	++	++		The jury can still detect an untreated orange
5	4% NAG 141	10:20		+	=		++	+		
10		2:20	=	=		++	++	=		
15		4:20	+	=	=	-	+	+		
Average			-	=	=	+	++	-		- A slight diphenyl odor
Repeat the next morning										
3			-			-	++	+	=	
8						+	++	+	-	
13			-			+	++	++	+	

TABLE X

ODOR TESTS ON DIPHENYL MIXTURES IN JARS CONTAINING FRUIT

Chemical Added	Jury S	Mi	Ma	G	D	W	Conclusion
0.5% NO (1:2), 1.5% orange and							
2% E	=	=	+	+		++	Diphenyl odor
2% D	+	++	+	++			Sweet odor
2% F	-	-	=				Musty, stale
1% F and 1% J	+	+	++	+		=	Sweet odor
1% M and 1% J	=	++	+	+		=	Sweet odor
1% F and 1% E	-	+	+	+			Musty odor
0.5% NO (1:2), 3.5% A and 2% D	+	++		+		+	A little spice needed
Same as above with 0.5% M	=	++	=				Diphenyl odor
1% NO (1:2), 7% A	++	+	++		-		Pungent odor
1% NO (1:2), 6% A and 1% M	++		+	++	++		Orange odor
A alone added to orange, no diphenyl	++	++	++	++	++	++	Very good
A and M (4:1) added, no diphenyl	++	++					Better than A alone
0.2% NO (1:2), 6.2% A, 0.8% F and 0.8% M	++	++	++	++	+	+	Best yet
0.3% NO (1:2), 6.8% A, 0.9% of M and 0.1% J	+	++	++	++		+	These bring out the sweet odor too much
0.1% J and F (1:1)	+	++					

TABLE XI

ODOR TESTS IN 8-INCH BOXES FILLED WITH FRUIT

Chemicals Added	Jury							Conclusion
	W	A	S	Ma	Mi	G	D	
8% of NO-A-M P 1:28:4:4 mixture	+		+	++	+	++	+	Slight lime
8% of NO-A-M P 1:130:2:2 mixture	++	+	+	++	++	+	+	
8% of A M P 6:1:1 mixture	++	+	+	++		++	+	Pungent lime

Key to Table I -

A	lemon oil
B	orange oil
C	lime oil
D	eugenol
E	safrol
F	methyl salicylate
G	Ammomask
H	cyclohexyl acetate
I	fenchone
J	2-naphthyl methyl ether
K	isoeugenol
L	Neutroscent
M	morpholine
N	pinene
O	carvone
P	methyl phenylacetate
Q	octyl acetate
R	diphenyl ether (Dowtherm)
S	cyclohexanol

Key to Tables V to XI

A	orange oil
B	anise
C	citronellol
D	geraniol
E	verbena
F	spike
G	piperonal
H	eugenol
I	methyl phenolacetate
J	safrol
K	Yara-Yara
L	methyl anthranilate
M	lime oil
N	vanillin
O	coumarin
P	lemon oil