A STUDY OF PHYSICAL FACTORS WHICH INFLUENCE THE EFFICIENCY OF FLOUR BLEACHING WITH NITROGEN TRICHLORIDE

by

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B. S., Oklahoma A and M College, Stillwater, 1941

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Milling Industry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1949

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INTRODUCTION

At the present time the chemical compound nitrogen trichloride or "Agene" as it is known commercially, is the principal gaseous aging material used in flour mills[1]. In addition to the gaseous maturing agents, which may exert a considerable bleaching effect, millers usually add to the flour solid bleaching powders, the active ingredient of which is benzoyl peroxide. This material, bearing the trade name "Novadel", serves only to bleach the flour and does not exert any appreciable maturing action. If it were possible to increase the efficiency of gaseous bleaches in flour, a saving could be effected due to the corresponding reduction in the amount of the benzoyl peroxide required.

Since the efficiency of flour bleaching with gases depends on the flour agitators used in the process, it is an objective of the present studies to design a flour agitator exhibiting high efficiency. However, before such equipment can be designed, information on the numerous physical and chemical variables which influence bleaching will first need to be obtained. It is for this reason that the present research was undertaken.

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[1]On Nov. 2, 1948, the Pure Food and Drug Administration issued a preliminary order banning the use of nitrogen trichloride for flour bleaching. The final order became effective on Nov. 12, 1948, and the final date for the use of Agene will be Aug. 1, 1949. The reason for this change is that flour treated with Agene has been shown to be toxic to certain animals when fed in excessive amounts. Mellanby (1946), Silver et al. (1947), Newell et al. (1947).

REVIEW OF THE LITERATURE

Millers and bakers have known for many years that freshly milled flour shows an improvement in baking properties and yields bread of improved crumb color when allowed to age or mature in the presence of air for a few weeks. The exact chemical nature of the improving effect due to artificial or natural maturing agents is not clearly understood, although it is known that the gluten proteins are involved and that an oxidation of protein sulfhydryl groups to disulfide linkages is probably a basic mechanism in the aging process (Sullivan, 1948).

In contrast to the lack of specific information concerning the maturing effect, the decolorization of the pigments of wheat by oxidative bleaching agents is quite well understood. In the most recent study of this subject, Keng-Tao Chen (1945) found that the coloring matter of hard red winter, hard red spring, soft white and durum wheats consisted of the pigments xanthophyll, xanthophyll esters (the pigments esterified with various naturally occurring fatty acids), and carotene. The distribution of these pigments in various parts of the kernel of different commercial classes of wheat is shown in Table 1, which is taken from the data of Keng-Tao Chen (1945).

Among the early studies on factors which influence the removal of pigments from flour with natural aging in air, may be cited the work of Avery (1907) who reported that exposure to direct sunlight accelerates natural bleaching. Winton (1911) showed that the gasoline color value of flour (which until

Table 1. Carotene, xanthophyll and xanthophyll ester contents of endosperm, embryo, and bran of different classes of wheat.[2]

	Dry matter basis							
	Endosperm		Embryo		Bran		Whole wheat	
Class of wheat	µg/g	%	µg/g	%	µg/g	%	µg/g	%
Hard red spring								
Carotene	.09	5.7	.72	10.0	.04	4.3	.18	10.0
Xanthophyll	.84	53.5	5.78	80.3	.42	45.1	.99	55.0
Xanth. ester	.64	40.8	.69	9.6	.47	50.5	.63	35.0
Total	1.57		7.19		.93		1.80	
Hard red winter								
Carotene	.11	5.5	.80	10.2	.02	2.1	.21	10.3
Xanthophyll	.77	38.5	5.98	76.2	.33	34.8	.79	38.7
Xanth. ester	1.12	56.0	1.06	13.5	.60	63.2	1.04	51.0
Total	2.00		7.84		.95		2.04	
Soft white								
Carotene	.21	9.6	1.13	10.2	.03	3.4	.25	10.8
Xanthophyll	1.18	54.2	9.70	87.8	.32	36.4	1.33	57.8
Xanth. ester	.79	36.3	.21	1.9	.53	60.2	.72	31.4
Total	2.18		11.04		.88		2.30	
Durum								
Carotene	.08	4.1	.50	12.2	.10	4.5	.15	7.6
Xanthophyll	1.78	90.8	2.93	70.8	1.31	59.0	1.67	84.8
Xanth. ester	.10	5.1	.70	17.0	.81	36.5	.15	7.6
Total	1.96		4.13		2.22		1.97	

[2]Solvents were petroleum ether for carotene pigment, and diethyl ether for the two xanthophylls.

recently was a widely used method to determine the pigment content of cereal products) decreased gradually on storage of the flour in air for thirty weeks to a value of about one-third of the original. Monier-Williams (1912) found that flour would decrease in carotene content from 2.00 to 1.40 parts per million when stored in sealed cans for two months, whereas, if stored open to the air, the carotene declined to 1.12 parts per million. The bleaching obtained in both cases apparently involved atmospheric oxygen.

Kent-Jones (1924) studied the effect of storage on flour samples in a vacuum and in atmospheres of hydrogen and air. He reports that no bleaching occurred in the vacuum and very little bleaching in the hydrogen in comparison with the normal bleaching which took place in the air. The samples were stored over a period of two months.

Ferrari and Bailey (1929) found that flour stored in air at 0°C. would bleach only about one-half as fast as that stored in air at room temperature, indicating the temperature factor to be an important one. Surprisingly, flour stored in carbon dioxide at room temperature showed about the same rate of bleaching as in air at room temperature, which suggests that carbon dioxide did not retard the bleaching, and that oxygen was apparently occluded in the flour particles. These authors further showed that natural bleaching apparently follows a straight line function for a period of 310 hours. When chlorine was used as a bleaching agent, the removal of color from the sample was 90 per cent complete in the period of treatment.

Moreover, this flour continued to decrease in color steadily for 105 hours after treatment. Nitorgen trichloride acted similarly but showed less bleaching than did chlorine. The color removal from flour by nitrogen trichloride at optimum treatment leveled off after about 60 hours, whereas the same effect was shown by chlorine at lower concentrations. Novadel was added to the flour in two concentrations, 0.011 per cent and 0.0145 per cent. The pigment content of the sample at the lower rate of treatment dropped very rapidly over a period of two to three hours after which it began to level off. After 60 hours there was little or no decrease in the pigment content. The curve for color removal due to a higher chlorine dosage was similar, but it did not level off until after 160 hours. The difference in the pigment value of the flours tested at these two levels was only two parts per million after the color removal ceased.

Samples treated with Novadel at different concentrations bleached to approximately 60 per cent color removal in a period of from 153 to 197 hours. The larger dosages of Novadel caused more rapid initial color removal than did the lower dosages, but the latter removed just as much color as the larger ones if the time allowed for the reaction to proceed was sufficiently prolonged.

Similar experiments were carried out with flour made from Marquillo wheat, selected for experimental study because of its high initial color content of 4.56 parts per million. Results with such flours were very similar to those already given, when compared as to relative color removal.

This study indicated chlorine to be the most effective in removing color, while nitrogen trichloride and Novadel, respectively, were less effective.

Ferrari and Bailey (1929) also report the results of experiments in which flour was subjected to ultra-violet light. This radiation was an effective but inefficient method of bleaching, the inefficiency being due to the mechanical difficulty of irradiating all of the flour for a sufficient length of time to produce the desired bleach.

Ferrari and Croze (1934) carried out further experiments with ultra-violet light, using it to accelerate the action of Novadel. Irradiation of the flour with ultra-violet rays showed a definite increase in rate of bleach, but this procedure was not considered commercially feasible because the flour turned slightly brown due to other effects of the radiation. Furthermore, the process did not lend itself readily to the continuous processing techniques used in flour mills, even though it was possible to reduce the time for maximum bleaching effect from 24 hours to 30 to 50 minutes.

In a comprehensive study of the relationship of protein level to artificial aging, Rich (1934) treated Canadian spring wheat flours of different protein content with various levels of nitrogen trichloride, beta-chlora, and potassium bromate. Flours of the following protein content were used: 10.7 per cent; 11.9 per cent; 12.4 per cent; 13.5 per cent; 14.2 per cent; and 15.3 per cent.

Rich's data, obtained when nitrogen trichloride was applied to the two flours of lowest protein content (10.7 and 11.9 per cent), indicated a detrimental effect to loaf volume. The flour containing 12.5 per cent protein was unaffected in loaf volume, whereas definite improvement in volume was obtained in the flours of higher protein content. Composite baking scores similarly reflected the negative effect of nitrogen trichloride on the loaf volume of low protein flours and the improvement which appeared with increasing protein content.

Beta-chlora (0.5 per cent nitrosyl chloride and 99.5 per cent chlorine) was slightly detrimental to flour at all protein levels as reflected in both loaf volume and baking score.

The series baked with potassium bromate showed similar but more pronounced trends to the series treated with Agene. The influence of storage on flour after Agene treatment was also studied. The flours of low protein were detrimentally affected by the storage in both loaf volume and baking score. The samples of high protein content showed a definite improvement in the case of unbleached flours, but only a slight improvement in the case of the Agene bleached flours. Rich states that the improving action of potassium bromate appears to be similar to that of nitrogen trichloride.

Ferrari et al.(1945), in the comprehensive study of the utility of various bleaching agents used singly and in various combinations, have found that the gas chlorine dioxide, when applied in an amount which yields optimum baking results, usually removes more color than nitrogen trichloride when used at an optimum baking level. Parker[3], on the other hand, has found chlorine dioxide to be less effective in color removal than nitrogen trichloride.

Ferrari and his co-workers (1945) found that commercial bleaching was less efficient than pilot-scale bleaching which, in turn, was less efficient than laboratory batch bleaching. The partial pressures of the gaseous reagent in the gas-air mixture going to the agitator was found to be a factor influencing the bleaching efficiency of nitrogen trichloride. Lower pressures gave more efficient color removal up to a certain point, beyond which there was no further improvement. Nitrogen peroxide, however, showed no difference in bleaching efficiency due to differences in partial pressures. These workers found that addition of the gas in small increments gave better efficiency in color removal than was obtained by adding all the gas in one dose.

Hutchinson, Ferrari, and Derby (1947) applied various combinations of bleaching gases to flour. The following are arranged in the order of decreasing efficiency:

Nitrogen trichloride followed by nitrogen peroxide
Hypochlorous acid followed by nitrogen peroxide
Chlorine dioxide followed by nitrogen peroxide
Chlorine followed by nitrogen peroxide

For pilot and commercial bleaching, each gas was applied in

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[3] Private communication from Dr. H. K. Parker, Wallace & Tiernan Co., Inc., Newark, N. J.

a separate agitator in the above order. The bleaching combination of chlorine dioxide and nitrogen peroxide seemed to be the most efficient of the gaseous bleaches but not quite as efficient as nitrogen trichloride followed by benzoyl peroxide which was used as a standard. Hutchinson and co-workers (1947) found also that nitrogen trichloride and chlorine dioxide, when applied to flour simultaneously in the same agitator, gave about the same results as when applied in different agitators with the chlorine dioxide being applied first. The following sequences were found to be the most effective for the gases studied in this report, in the order of decreasing efficiency:

Chlorine dioxide followed by nitrogen trichloride

Chlorine followed by nitrogen trichloride

Hypochlorous acid and nitrogen trichloride exhibited no preferential sequence. Ferrari snd co-workers (1947) believe that bleaching with three gases does not seem to be commercially feasible since it offers no advantages from the baking improvement standpoint.

A number of variables which probably influence the treatment of flour with nitrogen trichloride and other gases have not been investigated. Among these may be included time of treatment, temperature, moisture content, loading of the agitator, protein content of the flour, and variety of the wheat from which the flour was milled. The manner in which flour is mixed with itself and with the bleaching agent is also probably of great importance. With the objective of providing the basic information necessary for the design and operation of improved bleaching processes, an experimental study of the influence of these variables was carried out in this research.

MATERIALS AND METHODS

Agitator for the Laboratory-Scale Experiment

A small batch type agitator was constructed from wood as shown in Fig. 1. It was believed that this design would provide better agitation than the standard square box agitator furnished by the Wallace and Tiernan Company. The box of the agitator was octagonal in cross-section. The inside dimensions were: width, 8½ inches, and length, front to back, 12 inches. Each of the eight sides was 5 inches long with a thin paddle 1½ inches deep running the full width of the box perpendicular to the side which supported it. The agitator was rotated by a fractional horsepower reducing gear motor with a belt and pulley drive at 29 revolutions per minute. The means of closing the box by a catch was the same as is used on the box of Wallace and Tiernan.

Method of Generating Nitrogen Trichloride

To generate nitrogen trichloride the equipment in Fig. 2 was used. The desired amount of chlorine was measured into Buret A, which had a leveling bulb attached. Saturated sodium chloride solution was used as the gas-retaining fluid in the buret and bulb since it absorbs very little chlorine. The chlorine was forced into ammonium chloride solution in the reaction cylinder C, through the ceramic diffuser D, under pressure. Stopcock E was closed and stopcock G was opened to supply air to the

Fig. 1. Flour agitator mounted in cabinet with temperature and humidity control.

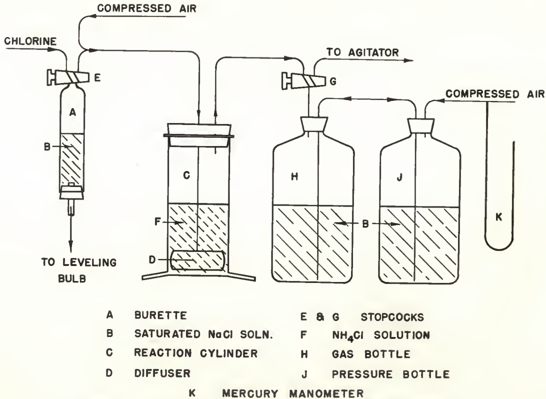


Fig. 2. Schematic diagram of NCl_3 generating equipment.

diffuser for aerating the Agene into bottle H. Sufficient time (4 minutes) and air (2.5 liters) were used in aeration to insure efficient removal of the Agene from the reaction solution. The equipment was calibrated to determine the exact pressure required, as indicated on a mercury manometer, to displace the gas-retaining liquid from bottle J into bottle H thereby forcing the gas from bottle H into the agitator over a desired period of time, through a pressure regulator which was set for a predetermined pressure. The surfaces of the solution in bottles J and H were maintained at a common level by means of a pulley suspension system which insured a constant rate of flow of Agene to the agitator. The amount of chlorine to be used was calculated by means of the following equations:

(1) $3\ Cl_2 + NH_4Cl \longrightarrow NCl_3 + 4\ HCl$

(2) 1 gram NCl_3/cwt. = .01 grams NCl_3/lb.

(3) .01 grams NCl_3 = 1.86 ml NCl_3

(4) (1.86)(L)(G) = ml NCl_3

L = pounds of flour to be bleached

G = rate in g/cwt. at which the flour is to be bleached

From equation (1) it readily can be seen that three volumes of Cl_2 are required to produce one volume of NCl_3.

Therefore, (ml NCl_3)(3) = ml Cl_2 to be used.

Determination of Carotinoid Pigment Content

The extent of pigment removal was used as an index of bleaching efficiency throughout this work. The flour samples were allowed to stand approximately 24 hours after bleaching, before being analyzed. Determinations of pigment concentration were made using the water-saturated N-butyl alcohol extraction method of Binnington et al. (1941), the color being determined on an Evelyn photoelectric colorimeter. Results are presented as percentage color removal instead of the usual parts per million "carotene". The Pekar color test was used at first, but it was soon discarded because of lack of sensitivity.

Baking Procedure

The baking formula used was as follows:

	Grams
Flour (14% moisture basis)	100
Sugar	6
Milk	4
Salt	1.5
Shortening	3
Yeast	2
Water	68 ml

The doughs were fermented for three hours after mixing at 30°C. (86°F.), proofed for 55 minutes at the same temperature, and baked as a single loaf on each of two days. The data presented are averages for the two loaves. Optimum absorption and mixing characteristics for this particular flour were determined in a preliminary baking trial. Optimum absorption was found to be 68 per cent. Agene at 2.5 g per hundredweight with potassium bromate at 3 mg gave optimum improvement. The mixing time was found to be 2 5/8 minutes.

Flour

The flour used was straight grade, milled to approximately 68 per cent extraction from an average commercial mill mix of wheat containing 12.7 per cent protein. The chemical analysis of the flour was 0.43 per cent ash; 11.90 per cent protein, and 2.65 parts per million "carotenoid" pigments (14 per cent moisture basis) as determined by the procedure outlined in Cereal Laboratory Methods, 5th ed. (1947). This flour was used exclusively throughout this research. Three to four-hundred pound batches were milled on the college mill as needed. The flour was stored in air-tight containers in the cold room at 50°F. until used, in order to minimize natural oxidation and aging.

EXPERIMENTAL

Influence of Agene Treatment on Baking Properties

An important preliminary step was to determine which Agene treatment would yield optimum baking characteristics with the particular flour used in these experiments. Having such information, it would be possible to select, for the guidance of further experiments, an Agene treatment level which would yield good color removal in addition to the desirable aging effect.

Samples were bleached at the following Agene dosages (g/cwt.): 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 5.0, and 7.5. These samples were allowed to stand for about 20 hours after bleaching in order to allow the reaction to reach completion prior to color determinations and baking tests. The baking scores and loaf volumes obtained appear in Table 2, and a graph of the loaf volumes as related to Agene treatment is shown in Fig. 3. All samples were baked in duplicated, and the data presented are averages of these duplicates.

From Fig. 3 it appears that Agene caused no improvement in loaf volume at any level of treatment for this flour, and indeed dosages in excess of 3.5 g caused marked decreases in loaf volume. This absence of an optimum loaf volume is generally contrary to normal experience with Agene, but it is in line with the results of Rich (1934), who showed that flours containing less than 12.5 per cent protein were adversely affected in volume response. The flour used in this study had a protein content of 11.9 per cent. On the basis of these results, optimum Agene treatment was taken as 2.5 g since this level would be expected to cause good color removal and yet would not influence loaf volume adversely.

Relation Between Level of Agene Treatment and Color Removal

The influence of rate of application of Agene on bleaching efficiency in terms of destruction of pigment in the flour was investigated by analyzing for "carotene" samples which were treated at the following rates (g/cwt.): 1.0, 2.5, 5.0, 7.5, 10.0, and 20.0. The results of this experiment are presented in Table 3 and graphically in Fig. 4.

Table 2. Effect of Agene on baking characteristics.

NCl_3 treatment g/cwt	Loaf volume cc	$KBrO_3$ mg	Loaf characteristics Crumb color	Crumb grain
0	930	4	80	90
1	910	4	92	97
1½	915	4	93	96
2	900	4	99	98
2½	925	3½	99	98
3	910	3½	100	97
3½	920	3½	102	98
5	855	3	104	98
7½	840	2½	108	99

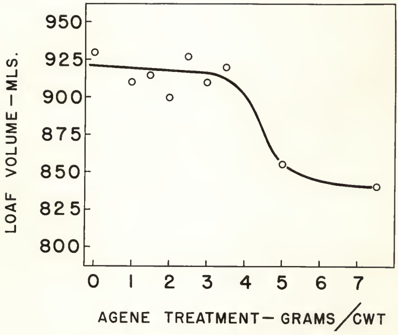


Fig. 3. Effect of Agene on loaf volume.

Table 3. Relation of Agene treatment to pigment content.

Nitrogen trichloride g per cwt	"Carotene", p.p.m.
0	2.65
1	1.73
2.5	1.00
5	0.73
7.5	0.65
10	0.65
20	0.63

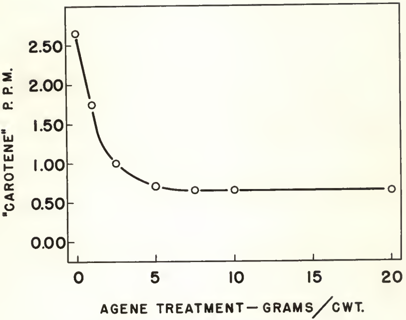


Fig. 4. Relation of Agene treatment to pigment content.

These data show that color removal is rapid and closely proportional to bleaching rate, for Agene treatment levels up to 2.5 g per cwt. In this latter region a very rapid decrease in bleaching efficiency appears with further increase in bleaching gas, and indeed no color removal below 0.65 ppm is obtained even when the treatment exceeds 7.5 g of Agene. It is clear that no further removal of pigment by Agene is possible below this value. This may indicate either that a very resistant residual pigment remains at this concentration or that a barrier to the penetration of the bleaching gas exists at a fixed depth in any flour particle, due possibly to the products of the reaction between Agene and the bleached pigments or another chemical constituent of the flour. No further data were obtained to account for this limiting level of carotene removal.

Influence of Time of Agene Treatment and Load on Bleaching Efficiency

Before work on the various physical factors involved in bleaching could be pursued, it was necessary to determine the minimum time of gas addition for maximum color removal as well as the influence of agitator loading on this variable.

Three series were bleached in order to determine the optimum time of treatment for three different levels of loading, with Agene at 2.5 g/cwt. The first series consisted of two-pound samples bleached over different time intervals. The second series consisted of four-pound samples, and the third series of six-pound samples. The times of treatment applied to the respective samples were as follows:

2-lb. samples		4-lb. samples		6-lb. samples	
Min.	Sec.	Min.	Sec.	Min.	Sec.
0	25	1	17	2	0
0	35	1	45	2	45
0	45	2	6	3	0
2	9	3	6	3	34
2	30	3	40	4	0
3	0	4	25	5	25
4	0	5	0	6	0

Eight and 10-pound samples were also bleached, but such excessive times of treatment were necessary to accomplish an optimum bleach as to make operation at this loading prohibitive.

The data obtained in this experiment are summarized in Table 4 and Fig. 5.

From Fig. 5 it can be seen that the curve for two-pound samples reached maximum efficiency in 45 seconds of exposure to the bleaching gas after which additional treating time produced no apparent increase in color removal. The four-pound loading reached maximum color removal in two minutes and 15 seconds of treatment. Maximum color removal was obtained by bleaching the six-pound sample for four minutes and 30 seconds.

Calculations may be made of the rate in pounds per hour at which each of these optimum bleachings occurred. Two pounds of flour bleached in 45 seconds is equivalent to 160 pounds bleached per hour. When four pounds of flour are bleached in 2 minutes and 15 seconds, the rate at which this proceeded was equivalent to 106.6 pounds per hour. Six pounds of flour were bleached to the maximum level in 4 minutes and 30 seconds, which was equivalent to a bleaching rate of 80 pounds of flour per hour. From

Table 4. Effect of load and time of treatment on color removal.

Load lbs.	Time Min.	Time Sec.	Initial "carotene" ppm	Final "carotene" ppm	"Carotene" removed ppm	Color removal %
2	0	25	2.63	1.25	1.38	52.5
	0	35	2.63	1.05	1.58	60.0
	0	45	2.63	1.03	1.60	61.0
	2	9	2.63	1.02	1.61	61.3
	2	30	2.63	1.04	1.59	60.8
	3	0	2.63	1.03	1.60	61.0
	4	0	2.66	1.03	1.62	60.9
4	1	17	2.60	1.24	1.36	52.3
	1	45	2.63	1.06	1.57	59.7
	2	6	2.66	1.04	1.62	60.9
	3	6	2.60	1.01	1.59	61.2
	3	40	2.63	1.03	1.59	60.8
	4	25	2.66	1.04	1.62	60.9
	5	0	2.63	1.03	1.59	60.8
6	2	0	2.63	1.26	1.37	52.0
	2	45	2.63	1.08	1.55	59.0
	3	0	2.63	1.06	1.57	59.7
	3	34	2.66	1.05	1.61	60.6
	4	0	2.66	1.05	1.61	60.6
	5	25	2.63	1.02	1.61	61.1
	6	0	2.63	1.03	1.59	60.8

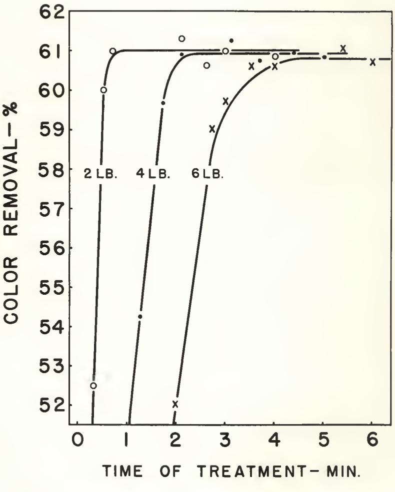


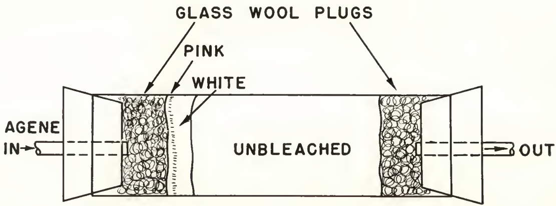
Fig. 5. Effect of load and time of treatment on color removal.

these calculations it is apparent that by increasing the load in the agitator the capacity with respect to time of treatment is not increased, but is in fact lowered. If this principle can be shown to apply to continuous agitators, it may well be an important factor in agitator operation.

From these data the two-pound sample loading with four-minute treatment was chosen for studying other variables. This apparently exeessive time of treatment would provide assurance that, when other factors were varied, any differences obtained could not be ascribed to time of treatment. Since the flour bleached at 45 seconda and that bleached at longer periods appeared to be identical so far as color content is concerned, there could seem to be no justifiable objection to choosing this time of treatment.

Effect of Agene on a Static Flour Plug

It appeared desirable to obtain an estimate of the velocity of reaction of Agene in flour as well as on the absolute maximum of pigment removal in the presence of a virtually unlimited quantity of Agene. For this experiment 150 g of flour were packed in a cylindrical glass tube between glass wool plugs and perforated rubber stoppers as shown in Fig. 6. A quantity of Agene mixed into 2400 ml of total gas (air plus Agene), sufficient to treat 150 g of flour at the rate of 60 g per cwt, was forced into the tube over a period of 10 minutes, with a pressure of 10 psi, the dilution air being allowed to escape to the atmosphere through the stopper at the opposite end.



EFFECT OF AGENE ON STATIC FLOUR PLUG

Fig. 6. Effect of Agene on static flour plug.

After passage of the gas, the flour plug appeared to have three distinct zones of color. The surface of first contact with the bleaching gas was slightly pink (Fig. 6), while immediately behind this was a white zone several millimeters in depth. A distinct line of separation existed between this white zone and the much larger bulk of apparently unbleached flour.

The flour was carefully pushed from the tube and separated into three fractions; the white zone comprising 15 g, a portion directly beyond the white portion also 15 g, and the balance of apparently unbleached flour.

The three portions of the flour plug were analyzed for pigment content with the following results:

Portion of flour plug	Fraction of total flour, %	Carotene ppm	Color removal %
White bleached zone	10.0	1.02	59.1
Intermediate zone	10.0	2.46	--
Unbleached zone	80.0	2.51	--

The apparently low rate of color removal of the bleached zone (59.1 per cent) is due to some intermixing of the bleached and unbleached flour when samples were being taken. The laminar nature of the bleached portion of the flour plug indicates that Agene acts with extreme rapidity since no irregular diffusion of the bleached area existed, in spite of the pressure applied to the gas to force it through the flour. Furthermore, it is significant that only 59.1 per cent of the total pigment was removed in the highly bleached area, which is only in the order of that obtained in the laboratory bleacher at considerably lower levels of treatment. The upper limit for the retention of Agene by flour is extremely high, but the extent of pigment removal is limited.

A simple calculation will indicate the speed of reaction of Agene with flour.

It can be shown that packed flour has about 52 per cent of free air space, leaving 48 per cent actually occupied by flour particles. Thus the cross sectional area of the tube, which is 2.036 square inches, would be made up of $2.036 \times \frac{48}{100}$, or 0.975 sq. inches of flour, leaving 1.06 sq. inches of intergranular space for gas flow. The volume of gas used was 2400 ml or 146.5 cubic inches, and the time of passage was 10 minutes. Thus the rate of flow through the flour cross-section was $\frac{146.5}{1.06 \times 10}$, or 13.8 inches per minute. Assuming that bleaching was complete in a zone 0.25 inch thick, the gas would pass through the bleached layer in only $\frac{13.8}{60 \times 0.25} = 0.92$ second.

This calculation shows that any portion of the gas reacted with the first 10 per cent of the flour plug within one second from the time of initial contact.

Mixing Efficiency

A characteristic of possible importance of a flour agitator is the efficiency with which flour is mixed with itself. To investigate this efficiency factor in the experimental agitator, a lot of the experimental flour was treated with an oil-soluble red dye, Sudan III. Equal samples of red and white flour were mixed, and the thoroughness of mixing was checked in 15 second intervals until judged complete by a flour slick test. The mixing of samples of one, two, and three pounds each of red and white flour was investigated in this manner. The results of this experiment are given in Table 5.

Table 5. Minimum time for complete mixing of different amounts of dyed and white flour.

Weight of each flour lbs.	Time for complete mixing sec.
1	30
2	60
3	120

The results show that a hyperbolic relation exists between total weight of a mixture and the time to secure homogeneous mixing. As load is increased, the time required for mixing increases very rapidly, thus indicating a marked loss of efficiency with excessive loading. For this particular agitator mixing rate is constant for loads of two and four pounds, but decreases for six pounds of load. It was indicated in a previous experiment that the minimum reaction time for a two-pound load with the bleaching gas was 45 seconds. Since 30 seconds were required for complete mixing of such a load, it appears possible that at lighter loadings, mixing is an important factor in bleaching efficiency.

Apparent Bleaching Efficiency Obtained by Blending Bleached and Unbleached Flour

The flour plug experiment has demonstrated the great rapidity with which Agene reacts with flour, and other experiments have shown that blending efficiency may be sharply reduced with overloading. Under certain conditions it is possible therefore that the gas intended to treat a certain quantity of flour may react with only a portion of the total amount, with the result that part of the flour will remain either only partially bleached or even entirely unbleached. Under practical conditions this could occur due to the use of periods of gas application which are too short to effect uniform distribution of the bleaching gas, with the result that the total bleach is not equally distributed throughout all the particles of flour. It was the purpose of this experiment to determine the influence on bleaching efficiency of such conditions.

A number of flour samples were treated with Agene to the following levels (g per cwt): 25, 12.5, 6.25, 4.7, 3.125, and 2.5. These bleached lots were then blended with unbleached flour to yield samples all containing 2.5 g/cwt of bleach, and were analyzed for carotene by the usual method. The data obtained are presented in Table 6 and Fig. 7. In Fig. 7 is also plotted values for final color obtained by calculation only, using the dilution factor of added flour. This followed the experimentally obtained curve very closely.

These results indicate clearly that overbleaching one portion of flour does not confer bleaching to unbleached flour mixed with it, and that the final color is an average of the two individual samples. The conditions of this experiment probably differ from those which occur commercially, only in that, in the latter case, one probably would deal with flour compounded of material underbleached to various degrees mixed with flour at various stages of overbleaching.

Table 6. Influence of mixing bleached and unbleached flour on apparent color removal.

Bleached flour in: mixture %	Nitrogen trichloride treatment (bleached flour) g/cwt	Carotene content of mixture ppm	Carotene removed ppm	Apparent color removal %
0	0	2.65	0	0
10	25	2.54	0.11	4.1
20	12.5	2.20	0.45	17.0
40	6.25	1.88	0.77	29.0
60	4.7	1.41	1.24	46.8
80	3.125	1.26	1.39	52.4
100	2.5	1.13	1.52	57.3

Effect of Temperature

A physical factor of possible importance to bleaching efficiency is temperature. To determine the effect of temperature on bleaching, the following experiment was carried out.

Identical four-pound samples of flour were sealed in glass bottles and brought to the following temperatures in the controlled constant temperature cabinet: 7°C., 15°C., 26°C., 40°C., 45°C., and 50°C. The various samples were bleached at these respective temperatures for four minutes at the standard rate of Agene treatment (2.5 g per cwt). The results, which are averages of duplicates at each temperature, are presented in Table 7 and Fig. 8.

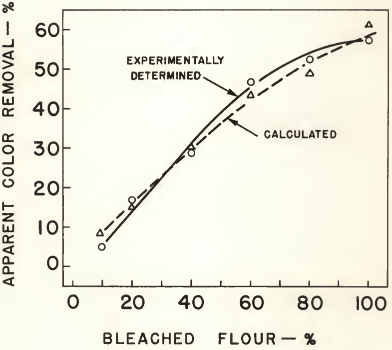


Fig. 7. Influence of mixing bleached and unbleached flour on apparent color removal.

Table 7. Effect of temperature on bleaching efficiency.

Temperature °C	Final* "carotene" ppm	"Carotene" removed ppm	Color removal %
7.5	0.93	1.72	64.8
15.0	0.96	1.69	63.7
27.5	0.98	1.67	63.2
40.0	1.00	1.65	62.1
45.0	1.03	1.62	61.2
50.0	1.06	1.59	59.7

*Initial carotene content 2.65 ppm.

The downward trend of the bleaching curve with increasing temperature as shown in Fig. 8 was unlooked-for in view of the fact that the rate of a purely chemical action can be expected to increase with an increase in temperature. Other explanations than purely chemical reaction phenomena must therefore be sought.

Gortner (1938) states that adsorption reactions are characterized by a negative temperature coefficient. This phenomenon would seem to be applicable to this curve.

It seems probable that adsorption precedes chemical reaction and therefore this initial interaction, which is negatively related to temperature, may be of primary importance in bleaching of flour with gases. Thus the more slowly the Agene was adsorbed, as at high temperature, the less efficient was the subsequent chemical reaction with the flour pigments. Differences in

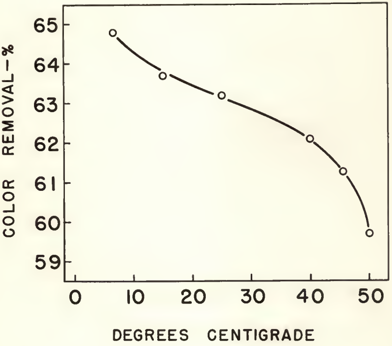


Fig. 8. Effect of temperature on bleaching efficiency.

bleaching efficiency occurred at low and high temperature in spite of the fact that the amount of Agene treatment was uniform at all temperature levels.

It is known that Agene reacts with at least three components of flour; namely, proteins, fats, and pigments. It may be that the velocity of chemical action of Agene on these compounds varies with the rate of adsorption. Evidently this change in the rate of adsorption affects the complex chemical reactions in such a way that more Agene eventually reacts with the pigment as the temperature decreases.

Effect of Temperature as Related to Time of Treatment

In the previous experiment, increasing temperature was found to decrease the efficiency of bleaching when the gas was applied over a period of four minutes. It was of interest to ascertain whether increased efficiency at the higher temperatures might be obtained if the time of gas treatment were extended. For this experiment a series was bleached over various time intervals at each of four temperatures; namely, 25°C., 31°C., 35°C., and 45°C.

A representative experiment was as follows. Ten sealed bottles of flour, which had been maintained in the cold room at 50°F., were placed in the constant temperature cabinet at 45°C. These samples were brought to this equilibrium temperature by holding in the cabinet over night before bleaching. The different times of Agene treatment at the various temperatures were as follows:

	Temperature							
	25°C.		31°C.		35°C.		45°C.	
	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.
Time		17		25		19		37
of		28		45		38		54
treatment	1	07	1	10		45	1	12
	1	40	2	0	1	18	1	45
	2	40	2	35	2	20	2	40
					2	50		

All samples were bleached in duplicate, and the data presented in Table 8 and Fig. 9 are averages of these duplicates.

The data of Fig. 9 indicate that at low temperatures; e.g. 25°C., maximum bleach is obtained at much shorter periods of treatment. However, as temperature is increased, the time required to produce maximum bleach is rapidly extended until at 45°C. the optimum bleach was reached only after three minutes as compared with one-half minute required at 25°C. Furthermore, this experiment confirms the previous one in that the maximum bleaching obtainable at any time was inversely related to the temperature.

The experiment proves conclusively that decreased temperature is related to increased efficiency both as regards time of gas treatment and maximum bleach obtainable.

Table 8. Effect of temperature and time of treatment on color removal.

Temperature °C	Time sec.	Final* "carotene" ppm	"Carotene" removed ppm	Color removal %
25	18	1.10	1.55	58.5
	32	1.00	1.65	62.2
	67	1.00	1.65	62.2
	100	1.01	1.64	61.9
	160	1.00	1.65	62.2
31	25	1.14	1.51	57.0
	45	1.08	1.57	59.2
	70	1.06	1.59	61.0
	120	1.05	1.60	61.5
	155	1.06	1.59	61.0
35	17	1.16	1.49	54.0
	30	1.11	1.54	56.0
	45	1.06	1.59	57.9
	78	1.01	1.64	59.9
	135	0.98	1.67	61.1
	167	0.98	1.67	61.1
45	36	1.20	1.45	53.8
	55	1.17	1.48	55.0
	72	1.13	1.52	56.5
	105	1.05	1.60	59.6
	160	1.02	1.63	60.8

*Initial carotene content 2.65 ppm.

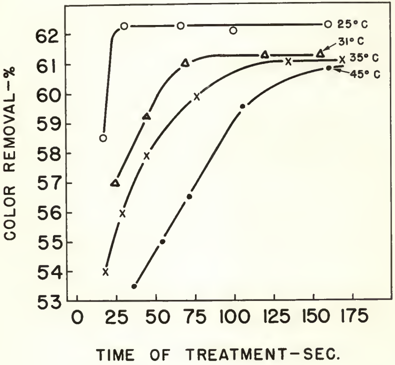


Fig. 9. Effect of temperature and time of treatment on color removal.

Effect of Moisture Content on Bleaching Efficiency

This experiment was set up to determine the effect of moisture content of the flour upon the bleaching efficiency. A group of flour samples with moisture contents ranging from 8.9 to 15.2 per cent were bleached with Agene at the rate of 2.5 g per cwt. Other factors such as bleaching time, temperature, and load were held constant in this experiment. The samples of lower moisture content were prepared by air-drying the flour sample at room temperature until the desired moisture content was reached. Moisture content was determined in a preliminary manner with the Patterson moisture meter, and precise moisture values were determined on the final samples by the A.A.C.C. air oven method. For higher moisture contents, the flour was spread out about one-half inch deep on paper in the humidity cabinet shown in Fig. 1. The relative humidity in the cabinet was maintained at approximately 99 per cent at a temperature of 45°C. At 15-minute intervals the flour was thoroughly stirred. When the desired moisture content was reached, a sample was sealed in an air-tight jar. For a moisture content of 15.2 per cent about four hours in the cabinet were required. The jars containing the flour samples of various moisture content were stored overnight in the cabinet maintained at 30°C. in order that all samples would be bleached at this common temperature. The results of this study appear in Table 9 and Fig. 10.

Contrary to the opinion generally held in the industry that bleaching efficiency increases with moisture content, exactly the

Table 9. Influence of moisture content on color removal.

Moisture %	Final* "carotene" ppm	"Carotene" removed ppm	Color removed %
8.98	0.82	1.83	68.9
10.60	0.85	1.80	67.7
11.80	0.91	1.74	65.5
12.25	0.93	1.72	65.0
12.85	0.98	1.67	63.0
13.70	1.02	1.63	61.1
13.80	1.03	1.62	60.9
14.60	1.05	1.60	60.3
15.20	1.06	1.59	60.0

*Initial carotene content 2.65 ppm.

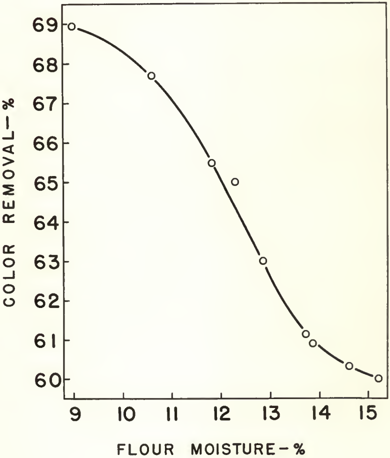


Fig. 10. Influence of moisture content on color removal.

opposite phenomenon was found to be true in this experiment. The data of Table 9 and Fig. 10 show that a decrease in bleaching efficiency occurred throughout the entire moisture range investigated; namely, 8.9 to 15.2 per cent, and that the greatest downward inflection of the curve for bleaching efficiency existed in the region of 12 per cent moisture. One possible explanation for this curve is the low solubility of Agene in water. As the moisture content in the flour increases, therefore, it is to be expected that its affinity for Agene would decrease. It can be seen from Fig. 10 that, in the normal commercial range of flour moisture; i.e., between 12 and 14 per cent, large differences in bleaching efficiency occurred.

Relative Efficiency of Experimental Agitator and the College Mill Agitator

Ferrari and co-workers (1945) stated that pilot scale bleaching is less efficient than bleaching on an experimental basis, and that the commercial bleaching process was even less efficient than that carried out on pilot scale. It was of interest, therefore, to compare the efficiency of the small box agitator with the Alsop agitator in the College mill. The latter was operated at a load of 500 pounds per hour, which is the normal production rate of the mill and which is very low for agitator equipment of this size. Using the commercial Agene generating and metering equipment, samples were bleached at the following rates (g/cwt): 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0. An unbleached lot of this flour was taken for treatment in the experimental agitator at the same rates using a loading of two pounds and a time of gas treatment of four minutes. The data obtained in both studies are given in Table 10 and Fig. 11.

The curves in Fig. 11 showed that no apparent difference existed in the efficiency of bleaching between the mill and experimental agitator. This result differs from those obtained by Ferrari and co-workers, who found the experimental type to be more efficient. It is probable in the present instance that the high efficiency in the mill bleacher was due to the fact that it was very lightly loaded. In any event, it is apparent that commercial equipment can be operated to yield optimum utilization of bleaching gas and that the proper technics of bleacher operation remain to be determined by research methods.

DISCUSSION AND CONCLUSIONS

The results of this study indicate that a number of variables influence the efficiency of Agene action on flour. In spite of the fact that this bleaching gas will soon no longer be used in American mills, the experimental results obtained here are pertinent to bleacher operation and gaseous treatment of flour generally, and should prove useful in improving the efficiency of such processes.

It has been shown that only small quantities of Agene are required for optimum maturing effect, and that treatments beyond 5 g per 100 pounds of flour are detrimental to bread characteristics. While no improvement in loaf volume was obtained by treatment of the flour used in these experiments, due apparently

Table 10. Comparative color removal of Kansas State College mill and experimental agitators at various levels of Agene treatment.

Equipment	Nitrogen trichloride g/cwt	Final "carotene" ppm	"Carotene" removed ppm	Color removal %
K.S.C. Mill Agitator	0	2.73	0	0
	½	1.70	1.03	38
	1	1.38	1.35	50
	1½	1.06	1.67	61
	2	1.03	1.70	62
	3	0.83	1.90	70
	5	0.85	1.88	69
Experimental Agitator	0	2.73	0	0
	½	2.30	0.43	15
	1	1.42	1.31	48
	1½	1.16	1.57	58
	2	0.98	1.75	64
	3	0.91	1.82	69
	5	0.80	1.93	71

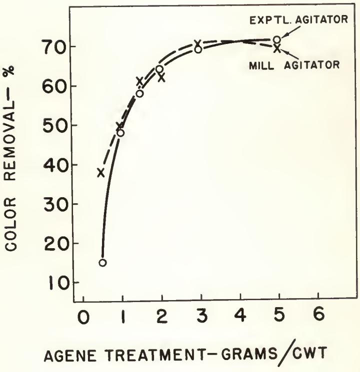


Fig. 11. Comparative color removal of Kansas State College mill and experimental agitators at various levels of Agene treatment.

to its low protein content and low oxidation requirement, it is generally agreed that increased loaf volume may accompany the use of Agene. It should be pointed out that Agene is used commercially primarily to improve the handling properties of bread doughs in the mechanical equipment employed in modern baking plants. Increased loaf volume and improved color are considered to be incidental to the basic maturing effect. Agene has an improving effect at low rates of treatment, though it is deleterious at higher rates of treatment. This is characteristic also of other oxidizing improving agents such as potassium bromate. The bromate effect, however, is otherwise different from that due to Agene since it appears to act principally in the baking process. It may operate independently of Agene in increasing the loaf volume of certain flours.

The great rapidity with which Agene reacts with flour was shown in the experiment using the flour plug. In spite of the extremely high rate of treatment (60 g per cwt), the Agene reacted with only a small portion of this flour (about 10 per cent). In spite of this very high rate of treatment, the color removal was limited to values no greater than the optimum amount removed by normal Agene treatment.

Studies by other workers (Ferrari, 1929) have shown that Agene is strongly retained by flour even though its influence on color removal is limited, as has been found in the present study. It seems probable that excessive Agene treatment reacts on the protein fraction of flour in proportion to the dosage applied, while only a limited portion of the Agene reacts with the pigments of the flour regardless of the extent of treatment above a certain point.

A number of purely physical factors which influence bleaching was investigated. It was shown by experiments involving the mixing of two flours of different color that, with increased loading of the agitator beyond the point of maximum efficiency, the time required for adequate mixing increased rapidly following a hyperbolic relationship. It appears, however, that efficiency remains constant at loading values below the point where decreased efficiency appears. It also was shown that the mixing of unbleached with over-bleached flour results only in an averaging of color of the two flours. No bleaching of the untreated flour is obtained by mixing it with an over-bleached sample. Another experiment along these lines indicated that the lightly loaded commercial bleaching agitator used in the long-system mill at Kansas State College bleached flour as efficiently as the box-type agitator used in the present experiments. It would seem that, under certain conditions of loading, commercial agitators may be operated very efficiently.

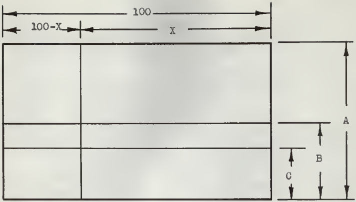
It would be desirable to express the efficiency of commercial bleaching with gases by a numerical value which would take into account the carotene content of the original unbleached flour as well as the maximum bleach which can be applied to the flour by the most efficient methods. The following determination and expression of such efficiency is proposed.

The maximum bleach would be that secured with the very efficient Wallace and Tiernan experimental box-type agitator. This value in ppm of carotene would be obtained by treating the unbleached flour with the gas at the same rate at which it was bleached in the commercial scale agitator. If the unbleached sample is to be stored or shipped prior to the test, it should be sealed upon collection in order to minimize changes in the moisture content. In any event, the sample must be bleached in the experimental bleacher at the same moisture content, temperature, and rate of gas application as was used in the commercial plant. Color content is determined as ppm of carotene by the method outlined in this report. By observing these details, a valid comparison of bleaching efficiency, unaffected by other variables, can be obtained.

The calculation of the empirical efficiency rating requires the assumption that the color value of the commercially bleached flour is an average of two lots of flour mixed together, one bleached to the maximum value obtainable in the experimental bleacher, and the other entirely unbleached. The calculation of efficiency, therefore, involves not only flour color in terms of ppm carotene, but also the relative quantities of the two flours (bleached and unbleached) in the mixture. Three color determinations, as follows, are the only analytical values which need to be secured:

1. The unbleached flour
2. The commercially bleached flour
3. Experimentally bleached flour

A geometric development of an equation for efficiency may be made with the aid of a diagram as follows:



Let A equal the color content in ppm of the unbleached flour.

Let B equal the color content in ppm of the commercially bleached flour.

Let C equal the color content in ppm of the experimentally bleached flour.

In this case, A is greater than B, which is greater than C.

X equals that portion of the commercially bleached flour, expressed as percentage, which contains the maximum bleach.

100 - X equals the percentage of unbleached flour in the commercially bleached sample.

Area due to commercially bleached flour equals 100B.

This area is equal to the sum of the areas CX - A (100 - X).

Equating these values:

$$100B = CX - A\ (100 - X)$$

Solving for X:

$$X = 100 \times \frac{(D - A)}{(C - A)}$$

The term X, which can be visualized as that portion of the commercially bleached flour, expressed in per cent, which contains a bleach value equivalent to that obtainable with the laboratory bleacher, might well be called the agitator efficiency, or simply AE.

Thus:

$$AE = \frac{(B - A)}{(C - A)} \times 100$$

As an example of the application of this equation, a practical case may be assumed where the unbleached, commercially bleached, and experimentally bleached flours have the following color values in terms of ppm of carotene, respectively:

A = 2.5

B = 1.2

C = 0.9

The agitator efficiency, or AE, of the commercial equipment in the case of this example can be obtained by substituting in the equation thus:

$$AE = \frac{(1.2 - 2.5)}{(0.9 - 2.5)} \times 100 = 80 \text{ per cent}$$

An important physical factor which affected Agene bleaching was temperature. Surprisingly, temperature was inversely related to efficiency. The decrease in efficiency obtained with increased temperatures indicates the possibility that adsorption of Agene by flour precedes its chemical action. Although at any two temperature levels the amount of Agene absorbed is the same, if the total dosage is identical, it was shown that at the lower temperature a greater degree of color removal was obtained. It would seem, therefore, that as the velocity of chemical reaction of Agene is increased, as by an elevation of temperature, the less is its efficiency in bleaching. At elevated temperatures, optimum bleaching could be obtained if the time of treatment were extended.

A particularly interesting result was that which indicated bleaching efficiency with Agene to be reduced as the moisture content of the flour was increased. These data are in contrast to popularly held opinions among millers to the effect that higher moisture in flour may result in more efficient utilization of the bleaching gas. The results obtained in this study, however, are to be expected if it is recalled that Agene is only slightly soluble in water and is preferentially soluble in fats and fat solvents. Moisture in flour would, therefore, tend to inhibit Agene up-take. It appears highly possible that the differential action of various bleaching gases such as chlorine, chlorine dioxide, nitrosyl chloride, etc., may be related at least partially to their solubility characteristics.

It is planned to continue the present studies to include investigations of other variables on bleaching efficiency using both Agene and chlorine dioxide. Factors such as protein content of flour, variety of wheat, flour granulation, and flour grade will be studied. The relationship of results obtained with the experimental agitator to those obtainable with commercial type equipment will also be explored.

SUMMARY

A number of physical factors which influence the efficiency of flour bleaching with Agene as determined by residual carotene content were investigated, using an octagonal box-type experimental bleacher. The following results were obtained:

1. Color removal was closely proportional to bleaching rate for levels up to 2.5 g nitrogen trichloride per hundredweight. Higher levels of treatment were accompanied by a decrease in additional color removal, and significant color removal beyond 0.65 ppm could not be obtained.

2. The time required to produce a maximum color removal for various loadings was found to be proportional to the loading.

3. An approximation of the time of reaction of nitrogen trichloride with flour was obtained, and was found to be slightly less than one second.

4. Mixing efficiency was determined for this agitator at various loadings and found to be closely related to bleaching efficiency, particularly at lighter loadings where reaction time was comparable to mixing time.

5. Temperature was shown to be inversely related to bleaching efficiency.

6. Bleaching at low temperatures was found to be more efficient with respect to both color removal and time of treatment.

7. An increase in moisture content was found to decrease the efficiency of color removal to a considerable extent.

8. A simple method for determining the quantitative efficiency of a commercial agitator is presented.

ACKNOWLEDGMENTS

The author wishes to acknowledge the guidance and suggestions of Dr. Max Milner in this investigation and preparation of this thesis. The help of Dr. D. B. Parrish is much appreciated. The assistance of Mr. Gerald D. Miller in analytical technique and the cooperation of the staff members of the Department of Milling Industry aided greatly in the completion of this work. The author is indebted to the Wallace and Tiernan Company, Newark, New Jersey, whose financial assistance made this study possible.

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