THE USE OF OZONATED AIR FOR EXCESS MOISTURE REMOVAL IN STORED GRAINS

Thesis for the Degree of M, S. MICHIGAN STATE COLLEGE William Franklin Brandt 1952

thesis entitled

"Investigation of the Use of Ozonated Air for Excess Moisture Removal in Stored Grains"

presented by

William F. Brandt

has been accepted towards fulfillment of the requirements for

M.S. degree in Agricultural Engineering

Walte M. Callos
Major professor

Date December 4, 1952

THE USE OF OZONATED AIR FOR EXCESS MOISTURE REMOVAL IN STORED GRAINS

Ву

William Franklin Brandt

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Agricultural Engineering

THESIS

1/8/43 8

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor James S. Boyd who was the advisor for this project, who also in cooperation with Professor Walter Sheldon did some pilot work previous to the work of the author. The information and assistance obtained from these men deserves due credit.

Many thanks are given to Dr. Erwin J. Benne of the Department of Agricultural Chemistry for the many hours of consultation so willingly given concerning the problems of the chemistry involved in the determination of ozone concentration.

The advice and information obtained from Dr. Clark E. Thorp of the Armour Research Foundation of the Illinois Institute of Technology concerning the chemical problems of ozone determination is also greatly appreciated.

To Dr. Chester A. Snell of Foster D. Snell, Inc. of New York, consulting chemists and engineers, a hearty thanks for more answers to chemical problems.

Acknowledgment is due to Dr. Walter M. Carleton whose comments and suggestions in preparation of the manuscript were very helpful.

Sincere appreciation for the financial support and use of equipment of the Electroaire Corporation is expressed by the author; for thus was it possible to carry on work in the quest of information that is vital to agriculture.

THE USE OF OZONATED AIR FOR EXCESS MOISTURE REMOVAL IN STORED GRAINS

Ву

William Franklin Brandt

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Agricultural Engineering

1952

Approved Walter M. Culitis

The harvesting of most field crops is dependent on the prevailing weather conditions at the time of harvest. The problem of how to handle crops that contain excess moisture has been with us for a long time and probably will always be a major problem in agriculture. However, experimental work is constantly being done to improve the present processing methods in order to prevent or reduce what is in many cases a severe economic loss.

In crop processing and storage the problem of excess moisture content is one of moisture removal to a safe level or treatment by some means which will reduce or eliminate the undesirable results which are caused by the excess moisture. Some time ago the application of a gaseous mixture of ozone and air to Brazil nuts seemed to indicate that there was an inhibition of mold and a very rapid loss of moisture in the nuts. This led the manufacturers of some ozone generators to believe that possibly the action of drying was accelerated appreciably by the addition of ozone to air. The next step was to test the hypothesis that ozone influenced the drying rate of various products. Experimental drying of several agricultural products was suggested in which the excess moisture problem seemed most troublesome. This particular project was conducted with white pea beans that contained excess moisture. However, shelled yellow dent corn was also used at first, the intent of its use being to become familiarized with the operation of the various pieces of apparatus involved. Data from all corn and bean drying tests are, however, included in the report.

Air at room conditions was forced at a controlled rate through a control bin of the material to be dried. Simultaneously a second bin of the same material and initial moisture content was treated with an equal unit flow rate (c.f.m./bu.) of an ozone-air mixture. Both bins contained the same initial weight of material. A total of four drying tests was conducted, the first two with shelled corn and the remaining two with white pea beans. One corn test and one bean test was conducted with the ozone generator operating at an output less than capacity while the other corn and bean test utilized the maximum recommended setting of the generator.

In analyzing the resulting data no significant increase in drying rate appeared in the treated bin, either for maximum or less than maximum output of the ozone generator. From laboratory germination tests there does appear to be some indication that ozone can be used as a fungicidal agent. There appeared to be a slightly smaller amount of mold growth on the seed coats of the germinating beans which were treated with ozone. However, the number of observations of moldy samples were insufficient to give any conclusive results. Possibly much higher concentrations of ozone are necessary than were obtained to cause effective fungicidal action.

TABLE OF CONTENTS

	Pag€
INTRODUCTION	1
OBJECTIVES	3
REVIEW OF LITERATURE	4
General Information	4
Theory of Drying	5
Results of Previous Experiments	10
Without Ozone	10
Properties of Czone and Its Uses to Date	13
EXPERIMENTAL APPARATUS	18
PRESENTATION AND DISCUSSION OF DATA	31
Laboratory Drying Test	31
Edibility Tests	58
CONCLUSIONS	60
APPENDIX I	61
APPENDIX II	65
Ozone Concentration Determination	65
APPENDIX III	77
LITERATURE CITED	86

LIST OF FIGURES

Figure	•	Page
1.	Fan and Ozone Generator Arrangement	19
2.	Orifice Plate Assembly	20
3.	Bins on Scales and Exhaust System	22
4.	Trier with Insert in the Closed Position	23
5.	Trier with Insert in the Open	
	(Sampling) Position	23
6.	Eight and Twelve Point Electronic Recording	
	Potentiometers	25
7.	Ozone Absorption System	26
8.	Titration Apparatus	29
9.	Thermocouple Locations in Air Drying (Control)	
	Bin of Corn Test No. 1	32
10.	Drying Rates of Corn Drying Test No. 1	34
11.	Net Weight Loss Comparison of Corn	
	Drying Test No. 1	39
12.	Thermocouple Locations in Air Drying (Control)	
	Bin of Corn Test No. 2 also Bean Tests	
	No. 1 and No. 2	41
13.	Drying Rates of Corn Drying Test No. 2	43
14.	Net Weight Loss Comparison of Corn	
	Drying Test No. 2	44
15.	Drying Rates of Bean Drying Test No. 1	46

	V111
Figure	Page
16. Net Weight Loss Comparison of Bean	
Drying Test No. 1	48
17. Drying Rates of Bean Drying Test No. 2	49
18. Net Weight Loss Comparison of Bean	
Drying Test No. 2	51
19. Field Emergence Test	52
20. Comparison of Plants in Block 2	54
21. Laboratory Germinated Beans - Air Treated	57
22. Laboratory Germinated Beans - Ozone Treated	57

23. Air Flow Through a Thin Plate Orifice......

64

LIST OF TABLES

Table		Page
I	Analysis of variance of the wet bulb	
	temperatures in the air treated bin of	
	corn drying test No. 1	35
II	White pea bean emergence in the field eight	
	days after planting	53
III	Analysis of variance of field emergence test	
	for white pea beans	54
IV	White pea bean germination in the laboratory	55
V	Analysis of variance of the laboratory	
	germination tests of white pea beans	56
VI	pH change of potassium iodide with	
	buffer additions	69

LIST OF TABLES

IN APPENDIX III

Table		Page
I	CORN DRYING TEST NO. 1	
	Control Bin - Air Dried	78
II	CORN DRYING TEST NO. 1	
	Test Bin - 03 & Air Treated	79
III	CORN DRYING TEST NO. 2	
	Control Bin - Air Dried	80
IV	CORN DRYING TEST NO. 2	
	Test Bin - 03 & Air Treated	81
V	BEAN DRYING TEST NO. 1	
	Control Bin - Air Dried	82
VI	BEAN DRYING TEST NO. 1	
	Test Bin - 0 ₃ & Air Dried	83
VII	BEAN DRYING TEST NO. 2	
	Control Bin - Air Dried	84
VIII	BEAN DRYING TEST NO. 2	
	Test Bin - O- & Air Dried	85

INTRODUCTION

The problems involved in the handling of farm crops that contain an excess amount of moisture are present each year in many sections of the United States, including the Michigan area. Both the forage and grain harvest seasons rarely escape the influence of unfavorable weather conditions. The excess moisture is not the direct cause of the storage problems but is of the indirect type in that it provides one of the necessary conditions which are highly favorable to the development of undesirable organisms, both plant and animal.

The two methods of moisture removal are (1) natural drying in the field and (2) the various artificial means. The commonly used artificial means to date are (1) naturally forced air through bins which depends entirely upon wind velocity pressure and bin construction to utilize that method, (2) fan forced natural air without heat added, and (3) fan forced air that is heated to some temperature above that of the natural atmospheric temperature.

During the past several years there has been an increasing interest in the applications of ozone (0_3) . This interest has been promoted to a large extent by the manufacturers of ozone generators. The first applications recorded were not in any of the fields of agriculture. More

recently the possibilities of applications in agriculture have been recognized. The work done on agricultural products to date has been chiefly in the field of refrigerated food storage. The results of some of the experiments conducted have been published and were of particular interest in this project. Some of the techniques described were useful in the organization and operation of the experimental equipment. The conclusions drawn in the past experiments were very helpful in understanding more fully the characteristics of ozone and the effects of its action.

OBJECTIVES

In this project the chief interest was in the processing of white pea beans containing moisture in quantities greater than that which can be safely tolerated in prolonged bin storage.

The first and main objective of this project was to test the hypothesis that ozone mixed with air would effect an increased rate in moisture removal when compared to the effect of air alone passing through the moisture laden material at the same flow rate, initial temperature, and relative humidity conditions. The second objective was to determine if the edible quality of white pea beans would be affected by being subjected to an "air" flow that contained ozone. The third objective was to check the germination of white pea beans in the laboratory and also emergence in the field for both the air and air-ozone treated beans.

On several occasions throughout the experiment specific difficulties became apparent. In some cases the difficulty was eliminated while in others it was not. Those problems encountered will be discussed in the appropriate place in the text and conclusions made will take them into consideration.

It is the hope of the author that the information presented and the experimental data obtained will be useful in further work of this nature.

REVIEW OF LITERATURE

General Information

Conditioning and storage are very important steps in grain production and marketing. Quisenberry [17] states that it has been estimated by the Food and Agriculture Organization that the present world losses of grain in storage amount to about twenty-six million metric tons, roughly equivalent to 950 million bushels of wheat per year or about 5.6 percent of the total cereal production of forty-eight of its member countries. In the United States the loss may be as high as 10 - 15 percent. The causes of these losses are due to insects, rodents, fungi, other microorganisms, and living processes in the grain itself. All losses except those due to rodents are very much dependent on the moisture content of the grain and the prevailing temperature conditions. It is generally agreed that microorganisms which are always present in large numbers on grain are the primary cause of deterioration in storage. Biological or chemical activity of the grain itself is not a large factor. As the moisture of the grain is increased its respiration does increase, but not at as rapid a rate as does the fungi respiration. Some work by Carter and Young indicates that heat damage in storage can be entirely accounted for by the released energy due to fungi respiration in and on the kernels. This heat generated must be removed

by some means or a self-accelerating process of temperature increase will take place until the stored grain is unfit for consumption. Kelly [15] states that there are only two problems to be solved -- the dissipation of heat and the removal of moisture before material damage has occurred.

Theory of Drying

Drying of a material takes place when there is a flow of moisture out of that material. For such moisture movement to occur there must be some force to produce that movement. As explained by Fenton [10], many of the problems connected with the drying of grain become clearer when approached from the standpoint of vapor pressures. A difference in vapor pressures between the grain and surrounding atmosphere will cause a moisture movement, either into or out of the grain. Grain temperature is of greatest importance in affecting vapor pressure and is the greatest single factor in grain drying. Vapor pressures within a grain increase at an increasing rate as the grain temperature is increased. Grain moisture content also affects the vapor pressure but is of much less importance than grain temperature. The vapor pressure of a grain at one temperature changes somewhat up to approximately 20 percent moisture content, but for higher percentages the same grain, for all practical purposes, will act like a free water surface.

Two principles of grain drying may be stated as follows:
[10]:

- 1. Grain gains or loses moisture because of the vapor pressure difference between the grain itself and the surrounding air. If the vapor pressure of the grain is higher than the pressure in the space surrounding the grain, moisture will flow out of the grain. If the reverse is true, moisture will flow into the grain and there will be a gain in moisture content.
- 2. The rate at which a grain gains or loses moisture is roughly proportional to the magnitude of the vapor pressure difference which prevails between the grain and the surrounding space. This rate is affected by the resistance to the movement of moisture vapor set up by the surface layers of the grain.

Grains, like many other materials are hygroscopic and thus lose or gain moisture, tending to maintain an equilibruim condition with the atmosphere in which they are placed. A number of grains have been exposed to constant temperature and humidity conditions to determine their equilibrium moisture contents and the results are available in the Agricultural Engineering publication entitled, Engineering Data on Grain Storage [21]. This data is by no means as complete as it should be. Although equilibrium moisture contents are given for several relative humidities, all of them are for the same dry bulb temperature. More data of this type that would include a wide range of dry bulb temperatures would be very convenient and necessary if the idea of vapor pressure differential is to be applied in drying experiments. information in a graphical form would be simple and convenient to use. With grain temperature as the abscissa and vapor pressure as the ordinate, a series of curves similar to the

4

relative humidity curves of a psychrometric chart can be plotted, where each curve would represent a specific moisture content of the grain.

Occasionally, suitable vapor pressure differentials for drying can be utilized when favorable atmospheric conditions occur. Forced ventilation during warm periods of weather to heat the stored product followed by the circulation of cold air provides large vapor pressure differentials naturally. It is advantageous to utilize these natural conditions but they may not always be present when desired. Natural atmospheric conditions can probably be better utilized for such crops as corn which are harvested rather late in the season when there is a good possibility of sharp temperature changes. In the case of white pea beans, the harvest is in that particular part of the year when such favorable natural drying conditions are not available most of the time. A vapor pressure difference of 0.05 to 0.10 p.s.i. is sufficient for effective drying. When vapor pressure differences of this magnitude cannot be obtained naturally, some other means must be used to provide an effective difference. The material to be dried can be heated to increase its vapor pressure and the pressure of the surrounding water vapor must be kept low if rapid drying is to be accomplished. Although the relative vapor pressure of the air is decreased by heating it, the absolute pressure remains the same, provided no moisture is added or removed. Barre [2] emphasizes the fact that pressure

differences in drying with heated air are obtained by an increase in vapor pressure of the grain and not by a decrease in that of the surrounding water vapor. Drying is accomplished because the grain is heated, not because the air is heated. The pressure of the surrounding water vapor can be reduced by removing water vapor through the use of absorbents such as calcium chloride and silica gel which have low vapor pressures even at high moisture contents. Cold surfaces can also be used to remove water vapor by condensation and thus reduce the vapor pressure around the grain.

In evaporating moisture from grain it is necessary to supply the latent heat of vaporization. Evaporation from a free water surface requires approximately 1000 B.T.U. per pound of water evaporated, the exact amount depending upon the initial temperature from which evaporation takes place. Hukill [12] points out that water evaporated from a grain instead of from a free water surface requires more heat. addition to the heat of vaporization from a free water surface the heat of wetting must be resupplied when the grain is dried. In the case of grain sorghum at 10 percent moisture dry basis, the heat of wetting is about 120 B.T.U. per pound of water. In any case, the amount of moisture evaporated from the grain is proportional to the amount of heat delivered to it. In all cases where artificial heat is supplied, the percent of heat supplied that is used for evaporation is an important factor in the efficiency of the drying process.

The total available heat is the difference between the initial dry and wet bulb temperatures providing no heat is lost or gained as the air passes through the material that is being Full utilization of this heat is seldom realized and dried. thus the efficiency of heat use is in most instances less than 100 percent. When no heat is lost or gained in the storage bin and the exhaust air is saturated, the efficiency would be at a maximum. In a batch type of bin relatively high efficiencies can be obtained during the early part of the drying period where the drying air comes in contact with a sufficient amount of wet material. As the drying front proceeds to the exhaust side of the batch type bin the forced air contacts less and less wet material in the bin and as a result the exhaust air leaves the bin in an increasing drier In other words the heat utilization efficiency condition. drops and would reach zero when all the grain in the bin is at equilibrium with the moisture and temperature conditions of the air supplied.

The term drying front is used to define a section (usually in a batch type bin) where a transition from dry to wet material is present. When drying air is forced through a mass of wet material the drying of that material begins where the air enters and proceeds in the direction of the air flow. The drying front is not a distinct plane but rather a cross sectional area of a certain depth which can be defined by some specific moisture content limits. For example, the upper surface of the front in white pea beans may be 18% wet basis and the lower surface 16% wet basis when the movement of the front is upward in the bin. This drying front characteristic is usually well defined when low rates of air flow are used while a high flow rate produces more uniform drying throughout the mass of wet material.

Results of Previous Experiments

Without Ozone

Not a great deal of work in grain processing and storage was done before 1940. Research work of this nature increased significantly just before and during World War II. Increased production to meet the larger food demand of that time made the grain handling and storage problems more acute. Most of the work done was with rice, corn, wheat, and sorghums.

Kelly [15] compared different bins and ventilating systems by noting the grain (wheat) temperature changes in different parts of the bin, rates of moisture removal, the commercial grade of the wheat before and during the storage period, and the changes in fat acidity and percent germination. couples were placed at different points in the bin and read with a potentiometer. Air flow rates as low as one to one and one-half cubic feet per minute per bushel of wheat were considered adequate to reduce the moisture content of 18 percent wheat without damage when a few hours of reasonably dry weather were available each day as is usually the case in the western wheat areas. Approximately one-third or slightly more of most stored grain volume is air space. Therefore, the resistance to air flow is not large. Laboratory tests reported by Fenton [10] indicate that the rate of moisture loss continues to increase with air movements up to 1200 air changes per hour or 20 air changes per minute. The loss of moisture at this rate of air change was 0.33 percent per hour with a vapor pressure difference of 0.10 pounds per square inch. Just how rapidly

air must flow for most effective drying is difficult to determine. Apparently wind pressure ventilation cannot always be relied upon to deliver the quantity and quality of air to dry a grain of high moisture content sufficiently to prevent spoilage. Barre and Kelly [3] observed field shelled or combined corn of 17.5 and 21.0 percent moisture stored in two wind pressure ventilated steel bins. The moisture content of both bins dropped to about 16 percent by the latter part of April, but certain parts in the bin became musty and removal was necessary to prevent further deterioration.

Three cases of interest are given by Shier, Miller and Junnila [20] as follows:

- 1. One bin had a hardware cloth floor and it was filled to a depth of 3 feet with high moisture corn. It was a 10 foot circular metal bin with ventilation by means of a No. 1-1/2 Siroco blower which furnished 800 c.f.m. or about 10 c.f.m. per square foot of floor area. It established the fact that the amount and distribution of air was sufficient to give uniform temperature changes through all parts of the grain. This change in temperature obtained by ventilating continuously night and day is very important in drying with unheated air.
- 2. (Drying cob corn 6 to 7 feet deep in a bin) Steam coils raised the temperature of air inflow about 20° maximum above air temperature outside. The 20° temperature rise cut the high winter relative humidity in half, and the corn dried down to 9 or 10 percent moisture. Drying started in the bottom where the air entered. With 20 percent moisture in the corn, the drying zone progressed upward at a rate of about 6 inches per day. The moisture carried up from below exposed the corn in the top of the bin to a high relative humidity. The upper corn assumed a moisture content of about 20 percent. As mentioned, the temperature did not exceed 55 degrees in the top of the bin and no visible or observed spoilage occurred in the corn which was later fed.

A portable test bin, about 4 x 4 x 8 feet high, was equipped with a hardware cloth floor and filled with about 100 bushels of 20 percent moisture corn. bin was operated in a laboratory where the temperature of the air was between 70-80 degrees and the relative humidity was very low because outside air temperatures were normally at least 40 degrees lower than in the laboratory. A small blower forced about 30 c.f.m. of air per square foot of floor through the bin. Due to the high temperature and low relative humidity, the heat exchange in the corn caused a 25 to 30 degree temperature drop. The air escaping from the top of the bin was naturally saturated but did not exceed a temperature of 55 degrees. The corn in the top of the bin contained 20 percent moisture and was exposed to saturated air at 55 degrees for 10 days but did not develop any sign of spoilage or a musty odor. This corn also dropped to about 9 percent moisture content.

According to Claydon [6] the first ventilated bin grain drier built on a farm in England was described in the September 10, 1948, Electrical Review. Continuous forced ventilation was used with the air temperature raised about 10 degrees above atmospheric. With such a low temperature increase no continuous supervision was necessary for there would be no risk of damage by overheating or overdrying. An attempt was made to hold the relative humidity in the neighborhood of 60 percent. The heat was switched on at night and off in the day when the relative humidity had fallen to about 75 percent. It was found that drying without heat was impracticable in even a normal season where the late August and early September relative humidities averaged around 84 and 85 percent respectively because the equilibrium moisture content of the grain at these conditions is about 19 percent.

Low temperatures of the forced air result in slow rates of moisture removal while higher temperatures greatly accelerate the rate of moisture loss. Fast rates of removal are desirable but there is a limit to how fast moisture can be removed and the temperatures to which many grains can be subjected. Quisenberry [17] states that it is generally believed that corn also may be seriously injured by drying too rapidly or at too high temperatures. Ear corn has been dried at 190-200 degrees with no immediate visible damage, but shelling revealed shriveled, brittle, and discolored germ ends of the kernels. Chemical analysis and feeding trials showed no significant differences and gave inconclusive results respectively between artificially and naturally dried corn. Quisenberry states that others have indicated that corn should not be subjected to temperatures above 180-200 degrees if feed value is not to be impaired. Even lower temperatures are necessary when grain to be used for seed is dried. For seed corn a drying temperature of 100-110 degrees is recommended at the start when the moisture content is high and later 120 degrees is safe after some of the moisture is lost.

Properties of Ozone and its Uses to Date

Ozone is an extremely active oxidizing agent, capable of reacting with all the elements with the exception of gold and

some metals of the platinum group. Natural rubber under stress is readily affected by such low concentrations as 3 or 4 parts per million, whereas unstressed rubber is not appreciably affected by fairly high concentrations of 50 to 100 parts per million [1].

There seems to be some difference of opinion concerning the stability of ozone in the presence of moisture. Ewell [9] quotes Clement's statement that ozone spontaneously decomposes bimolecularly, particularly if water vapor is present, but at so slow a rate that this cause of disappearance is negligible compared with the monomolecular loss in the presence of oxidizable matter. On the other hand Huntington [13] says ozone is extremely unstable when in the presence of moisture or of any material which can be oxidized, although it will endure almost indefinitely in air that is dry and cool. Another practice to consider in the argument is the method used in gas analysis as described in chemical references where the gas containing ozone displaces distilled water in a special flask by allowing the flask to drain, thus drawing the gaseous mixture into the flask. If ozone decomposed so readily in contact with moisture this procedure would be obviously unreliable. In discussing some of the work with ozone in ventilation and water purification McCord and Witheridge [16] say that a high relative humidity is just as destructive to ozone after it reaches the room air as it is in the ozone generator itself. More ozone must be produced on humid days than on dry days if the ozone odor is to be kept at a comfortable and preceptible intensity. On a very dry day the amount of ozone delivered to a room must be held to a minimum to prevent accumulations of high ozone concentrations.

In fungi respiration studies the treatment of grain with fungicides has been considered as a solution. Quisenberry [17] believed that practical application at that time might be questioned because all that could be expected would be a slowing up of the rate of deterioration, not prevention.

Results of the use of ozone in apple storage as reported by Schomer and McColloch [18] of the United States Department of Agriculture state that the chief values of ozone in apple storage are its maintenance of a pleasant atmosphere in the storage room and the control of surface molds on packages and walls. Ozone did not control decay of apples nor did it reduce the infection of innoculated wounds. Ozone did, however, retard the rate of enlargement of the infected areas.

When grains are stored cool and fed or milled before warm spring weather, high moisture may not cause spoilage since temperatures below 50 degrees apparently discourage mold growth in grains containing no more than 17 or 18 percent moisture [20]. Ewell [9] states that ozone does not appreciably inhibit growth of bacteria upon food surfaces containing a large amount of moisture when the temperature is above 50 degrees F., unless such high concentrations are employed that the accompanying

•

deleterious effect of the strong oxidizing agent vitiates its advantages. It is highly undesirable to use oxidizing agents in the storages of certain food products. The most significant effect is the production of rancidity. Bacon, sausage, lard, cream, butter, dried eggs, mushrooms, meat, and bananas are injured by concentrations of 50 to 100 parts per million of ozone. A continuous exposure of butter to 3 parts per million of ozone will cause bleaching and rancidity to a considerable depth. Observations of Ewell and Moran have shown that a continuous ozone concentration of as high as 3.5 parts per million for months will not injure eggs. A continuous minimum of 0.6 part per million of ozone prevents mold growth on clean eggs. Air borne infection killed by ozone is very slight at low humidities, moderate at 50 percent relative humidity, and very high when the relative humidity approaches 100 percent. When stored products are not dehydrated there will always be a high humidity for a short distance from the surface. fore, the killing power of ozone can be obtained on some products even though the relative humidity of the surrounding air may be low [8].

Homan [11] exposed corn and sunflower seeds and seedlings to Tesla discharge to determine what effect there might be on dry and germinating seeds. The seeds and seedlings were suspended between the discharge points of the two plates for various lengths of time. In this position they were subjected to an intense high frequency field and a high concentration of

ozone. Exposure for 12 or more minutes of such treatment at a point distance of 4 centimeters and a frequency of 4,500,000 cycles per second produced adverse effects. The result was stunted plants, most of which did not continue to grow after 8 or 10 days. None of the seeds were killed outright by this treatment. Homan also noted that ozone in a sufficient concentration had a bleaching action on chlorophyll and it seemed reasonable to assume that such a strong oxidizing agent might accelerate respiratory or aging processes. It was decided to try the effect of different concentrations of ozone on the rate of ripening of green bananas and tomatoes. Results indicated that no change occurred in the rate of ripening. Ewell [7] states that ozone, to some extent, retards ripening by destroying the ethylene gas given off by many fruits when nearly ripe.

Thorp [22] quotes a report of Toul's work on the insecticidal power of ozone as follows:

Meal worms were immediately killed by 2.5 percent ozone; I percent ozone killed in 12 hours, 0.5 percent in four days, 0.1 percent in seven days, 0.08 percent did not kill in fourteen days but had a deleterious effect, and 0.05 percent had no effect.

EXPERIMENTAL APPARATUS

Two complete drying units were assembled. Each unit consisted essentially of a centrifugal fan, a duct connecting the fan with the bin, and a bin with an exhaust duct.

The fans used were not identical in size and blade construction but could be controlled to deliver equal volumes of gas. The small fan that supplied the control or air treated bin has blades that are forward curved while the large fan which supplied the ozone treated bin has blades of the backward curved type. The air flow control on the small fan was effected by means of a cut-off shield at the fan inlet. Control of flow rate of the large fan was obtained by completely sealing the inlet on one side, partial coverage of the inlet on the opposite side, and manipulation of the variable speed drive on the three phase motor. The small fan was powered by a single phase fractional horse-power motor. Many of the details are shown in Figure 1. The ozone generator was placed near the inlet of the large fan so that the products of the generator could be readily introduced into the inlet by means of a flexible tube. A variac on the ozone generator could be adjusted to vary the primary voltage of the generator transformer, thus controlling the high voltage of the secondary and the resultant quantity of ozone produced by the individual generating units which are in parallel



Figure 1 Fan and Ozone Generator Arrangement.

with the secondary side of the ozone generator transformer. A very small centrifugal fan on the ozone generator and the method used to meter the gas flow necessitated the introduction of the ozonated air at the large fan. From the standpoint of ozone stability it would probably have been more desirable to introduce the ozonated air closer to the bin. However, velocity in the duct was of such magnitude that the time required for a particle of gas to traverse the length of the duct was very short.

Air flow was metered with the aid of thin plate orifices.

The orifices were turned on a lathe to insure accuracy of the



Figure 2 Orifice Plate Assembly.

diameter and sharp edges which are essential to accurate flow measurement. Vena contracta taps were placed in the ducts and differential pressure (static) was read with a multi-range, differential, well-type manometer. Two rubber tubes from taps at each of the two orifices were connected at two common junctions which lead to the manometer. Spring wire clips were utilized so that both differential pressures could be obtained within a relatively short time. This was important because of the slight flow variation from time to time due to the action of variable draft in a chimney which was

part of the exhaust system. Although flow rates could not be maintained at a constant rate with this type of a system, they could both be equalized quite readily at or very close to the flow rate desired. The formula that was applied to calculate the gas flow through the orifices and an example calculation are shown in Appendix I. Placement of the vena contract taps and the determination of the flow coefficient are also described where the example calculation is given.

As the air or air-ozone mixture was discharged from the end of the duct it passed into the plenum chamber at the bottom of the bin. From this location the flow was distributed over the entire cross section of the bin, passed through a false floor constructed of galvanized screen and up through the crop being dried, being exhausted at the top of the bin through canvas ducts leading into a chimney. The question may immediately arise as to why an exhaust system of this nature was used. As a control measure it was necessary to prevent any possibility of the accumulation of ozone in the room which might occur if some ozone were to be exhausted from the ozone treated bin. The ozone present in the room could then recirculate through the control bin and possibly invalidate any results. As previously stated, the exhaust system introduced one feature that was not desirable. Due to chimney draft the gas flow rate was not always constant. However, a duct on each bin leading the exhaust into the chimney equalized both flow rates so that a comparison of



Figure 3 Bins on Scales and Exhaust System.

results could still be made without questioning the two rates of gas flow.

Both bins were placed on platform scales and the weight of the contents of each bin was determined periodically, assuming any weight loss to be water expelled from the material in the bin. However, this method was not used as the final comparison between the two bins with respect to moisture removal. During the first experimental drying test five screen wire baskets of shelled corn were placed in the plenum chamber where the gas flow first contacted the wet grain in the bin. The same number of baskets (five) of shelled corn

were also placed in the top layer of the corn. Periodically one basket was taken from the plenum chamber and one from the top layer of corn. Both were oven dried in an electrically heated and thermostatically controlled unit at 212° F until a constant weight was obtained. The percent moisture (wet basis) was then calculated and recorded with the time at which it was removed from the bin. This method could not be used to obtain moisture samples within the bin contents so a grain trier about three feet in length was obtained. Figures 4 and 5 show the trier (or sampler) which was used for all moisture samples that were obtained in the remainder of the drying tests.

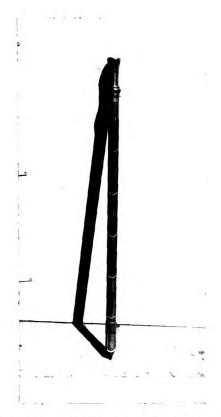


Figure 4 Trier with insert in the closed position.

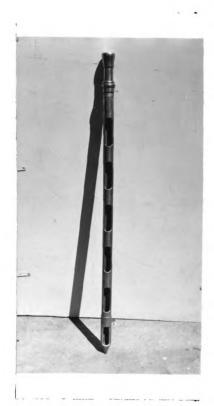


Figure 5 Trier with insert in the open (sampling) position.

During the second shelled corn drying test the grain trier was used but some inconsistent moisture determinations resulted. The grain trier used had no partitions in the inside section of the trier which allowed grain to enter the extreme top opening and possibly fall to the bottom of the tube if all other openings became bridged with damp grain. A change in the use of the trier to get samples for moisture determinations was necessary to eliminate the error caused by opening the entire tube length in the grain to be sampled. Instead of twisting the inside section which opens the holes in the entire length of the tube the inside section was positioned so that all openings were closed. The point of the trier was then driven to the position in the grain where the moisture sample was to be obtained. The inside section was then withdrawn from the outside section (without rotating it) until only the extreme bottom opening was open to receive a moisture sample. This eliminated the possibility of obtaining a mixed sample with its resultant To use a trier that has no partitions in the inside tube it is necessary to keep the trier well below the angle of repose for the material being sampled. A trier with partitions can be used at any angle from vertical to horizontal.

Temperature checks were made periodically at various points in the bin. To obtain these temperatures an aspirator type psychrometer and two potentiometer type, indicator-

recorder instruments were used. Copper-constantan thermocouples were placed at the same positions in both bins. An attempt was first made to record wet bulb temperatures at the bottom of each bin by applying a wet wick to a thermocouple. Upon checking the wet thermocouple against the psychrometer wet bulb a marked disagreement was found. Wet thermocouples read as much as ten degrees Fahrenheit above the aspirator psychrometer wet bulb in the plenum chamber of both bins at the position where the gas entered from the duct. Dry bulb temperatures by both methods of measurement usually agreed, however. Consequently all determinations of relative humidity and vapor pressure were based on the readings of the aspirator psychrometer. The following photo shows the electronic instruments used for temperature indication and recording.



Figure 6 Eight and twelve point electronic recording potentiometers. (8 point on left - 12 point on right).

The placement of thermocouples is described in the presentation and discussion of data.

The equipment shown in Figure 7 was part of the apparatus used in an attempt to determine the concentrations of ozone in the gaseous mixture which was forced through the material in the test bin.



Figure 7 Ozone absorption system.

Two filtering taps were placed in the side of the test bin, one at the level of the bottom layer and the other at the level of the top layer of material that was to be dried. It was from these two positions that gas samples were with-

drawn with the object of possibly finding a marked difference in ozone concentration at the two levels due to the known activity of ozone on organic materials. The purpose of the filters was to prevent particles of soil and organic matter from entering the main elements of the system. A three-way stopcock was fused to each filter so that air from the room could first be drawn through the gas absorbing system, thus permitting adjustment to the desired rate of gas flow before the air-ozone mixture was sampled from the bin. A 180° turn of the stopcock valve at the beginning of a timed gas sampling period connected the absorption system with the gaseous contents of the bin. The gaseous mixture then flowed through the fritted glass filter, through the stopcock, through a rotameter type flow meter, and then through a series of gas scrubbing bottles. A vacuum chamber connected to the end of this system served as a pulsation damping device and partly as a flow rate regulator. The vacuum pump was directly connected to the vacuum chamber which had a two-way stopcock opening to the atmosphere. The adjustment of this stopcock controlled the amount of vacuum in the damping chamber and thus controlled, in part, the vacuum applied to the gas scrubbing bottles. Another two-way stopcock between the vacuum chamber and the scrubbing bottles was necessary to maintain flow rate control by utilizing only part of the vacuum chamber pressure. At the end of a timed sampling period the three-way stopcock on the filter

at the bin was switched back to its original position, allowing room air to enter the absorption system for a few minutes so that all the gas sample from the bin would be flushed from the system. All parts of the absorption system which ozone contacted were made of pyrex. All joints were ground taper connections of a standard size. No rubber connections could be used before the scrubbing tube that removed the ozone because such connections would be attacked and finally destroyed by ozone. For this reason the concentration determinations would be invalidated because the ozone that may have been present in the bin would have been used to oxidize the rubber before it had passed into the scrubbing bottle which absorbed it.

In metering gas flow with a rotameter type flow meter the specific gravity of the gas with respect to air at standard conditions must be known because the calibration curve for the flow meter is based on air at standard conditions (14.7 p.s.i. and 70° F.). A mercury U-tube manometer was first included in the system between the rotameter and first scrubbing bottle to determine the amount of vacuum on the gas as it left the rotameter but no readable amount of vacuum could be obtained with the flow rate used. The manometer was therefore excluded from the system and the pressure on the gas was assumed to be barometric pressure at the time of sampling. Gas temperature at the flow meter was obtained by a mercury thermometer which was fastened to the outside of the flow

meter, the thermometer being in contact with the body of the pyrex flow meter. Corrections of the gas volume could then be made to convert the measured volume to a volume at any other conditions by means of the general gas law.

After a measured volume of the gas sample was passed through the scrubbing bottles the contents of the scrubbing bottle which absorbed the ozone had to be titrated. Figure 8 shows the equipment necessary to make such a titration.



Figure 8 Titration apparatus.

This chemical gas analysis procedure appeared at first to be the only reliable method for determining the concentration of ozone in air. It was not until after considerable time was spent in trying to develop proper techniques that difficulties became quite apparent. It has been found recently (some time after the experimental work of this project had been done) that the chemical procedure formerly accepted as the one that was most reliable is no longer accepted. Ewell [9] states that the use of ozone has been very seriously handicapped by lack of scientific quantitative methods both in research and in practice. Without knowledge of the actual concentrations of ozone employed the results of tests of its use are of little value.

For a more complete discussion of this problem and more recent information on the chemical procedure see Appendix II.

PRESENTATION AND DISCUSSION OF DATA

Laboratory Drying Tests

To obtain the data for drying rate comparison between air and ozonated air two drying tests were run with shelled yellow dent corn and two with white pea beans. Data on bean drying was the main objective of the tests but two runs were first made with corn so that the operation of the drying equipment could be checked before the bean tests were conducted. Graphical data from all corn and bean tests is presented. Tabulated data from all four tests is placed in Appendix III. All graphical presentations are taken directly from the tabular data.

In Corn Drying Test No. 1 the eight point recorder potentiometer was used as a means of checking dry bulb readings of the aspirator psychrometer and also to obtain grain temperatures at two different locations in each of the two bins.

The positions of the thermocouples in the bins are shown in Figure 9.

During the process of drying data was taken at several intervals of time. The six unit ozone generator variac was set on eighty volts (primary) for this test. Dry and wet bulb temperatures were determined where the air entered the grain and immediately after it emerged. From the dry and

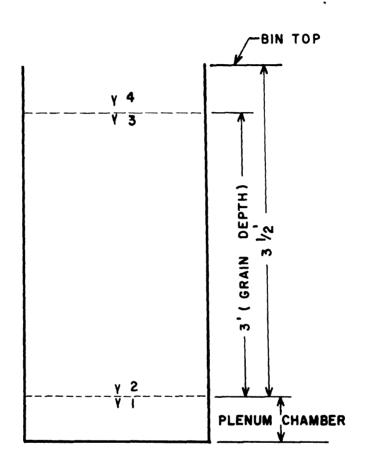


FIG. 9
THERMOCOUPLE (T.C.) LOCATIONS IN AIR
DRYING (CONTROL) BIN OF CORN TEST NO. 1.

NOTE: T.C.s in O_3 treated bin were in the same relative positions. Only the 8 point recorder—potentiometer was used in CORN DRYING TEST NO. 1. Therefore, point 5 in the O_3 bin compares with point 1 in the air bin, 6 with 2, etc.

wet bulb temperatures the relative humidities and water vapor pressures were read from a psychrometric chart. Moisture samples of the first corn drying test were obtained by placing corn of the initial moisture content (moisture content before any drying process was applied) in a number of screen wire baskets. These baskets of wet grain were then placed in the plenum chamber and also embedded in the top layer of corn in the bins. At intervals of time during the drying process baskets of the corn were removed from both the plenum chambers and the top layer of grain in the bins. These samples were then weighed and oven dried until a constant weight was obtained. The percent moisture (wet basis) was then determined for each sample. From these moisture determinations the rates of moisture removal are plotted as shown in Figure 10. A flow rate of 4 c.f.m./bu. of air and air-ozone mixture was used in all tests. Barre and Sammet [4] state that outside air might be heated 100 to 200 F., enough heat being used to reduce the relative humidity to about 30 percent. The heated air at the conditions just stated is usually forced through the grain at a rate of 2 to 4 c.f.m./bu.

The rates of moisture removal as shown in Figure 10 apparently show a slightly faster drying rate for the ozone treated bin. However, a statistical analysis of temperature and moisture conditions in the control and treated bins shows that ozone could not be entirely responsible for a more rapid drying rate. According to the theory of drying, the wet bulb

																							_	- 34	4 –		,
	: • . • ·	•			1						:		:					!									
1	-	· !		:			-			i	 	ļ			.			.	:							 	i
	-		ļ	!	`` - -					-		-		!	v			AYERS						09			:
	-			: -	:	:			• "	Ì .			•	1	TOP AVER	OF CORN			<u> </u>					-			
				-		:			· · · · · · · · · · · · · · · · · · ·	 					Ó	F		ROTTON	F						i i •		;
	-		-	-	-	-				-	-	-	-	-	-	_		111						3		-	
_ - - - - - - - - - - - - -		<u> </u>	:	•			•				. :. - 	<u> </u>		+==	== :			#									
						- -	 ر	1			4			-													
	-		-		-	//	1	<u> </u>	-	+		-	+	-	١.,	-				-		-		130	-		<u> </u>
				1.1		/	<u>:</u>					1	-		ļ				 							ļ:	
					11																						
			-	:	-	· i		-		-		-		-				-	-		-			<u>e</u>		-	<u> </u>
			-	-	1			-				-		-				1							T T T T T T T T T T T T T T T T T T T		
											1						1	1							-		0
		-	-	\prod	-			-		-		-		-		-	1	_		-		-		C	2		
													1		.l		/ /								1	1	FIG
																1	1				ļ		1111		AD. HIGTED		
	-		-		-			-	-	-		-	-	-	· ,	γ,	_							Ç	5		<u> </u>
			-													/				-							
							- : -:					-			1				10-	Ž	c						
	-		-	-	+	-				-	-	-	1	1.	<i>y</i>		-		U L	TFST	TREATER	TREATED		4 C			1 ::
+		-		-							· • · · · · · · · · · · · · · · · ·	/	/	 .					FAAT		-	1					
		-		 											<u> </u>				DEVING PATER AF	Ž	4	(5				
-	-				\downarrow	!		-		/	/	-	. i . i	-	<u> </u>				\ <u>\</u>	C		j		C		-	<u> </u>
-i											:			ļ						CORN DRYING	1						
			1		ن ا . ا		7						+														
	<u> </u>				1		-		: . · !			-												-c			
		- 4	}					C		· · · · ·				2			1	-	2				::. •	D			
										(SI	SAE	Ι.	3M	3	۱A.	\$14	W	%							 		
																								<u> </u>	•		

temperature should remain constant throughout the bin of material being dried. Providing no heat is lost or gained through the bin walls during drying a constant total heat process should be occurring; therefore, the wet bulb temperature should be the same on both the inlet and exhaust side of a bin. An example of the type of statistical analysis used is shown in Table I in which the wet bulb readings at the intake and exhaust of the control or air treated bin are compared. Sixteen wet bulb temperatures were recorded for the air at the inlet of the air treated bin in Corn Drying Test No. 1 and sixteen were recorded for the exhaust side. One wet bulb temperature at the air inlet and one wet bulb temperature at the exhaust side of the bin were determined at sixteen different times during the drying test.

In tabulated form the complete statistical analysis would appear as follows:

TABLE I

ANALYSIS OF VARIANCE OF THE WET BULB TEMPERATURES
IN THE AIR TREATED BIN OF CORN DRYING TEST NO. 1

Source	d.f.	S.S.	M.S.	F
Total	31	156.0		
Between	1	27.2	27.2	6.34*
Error	30	128.8	4.29	

F1,30 at the 5% level = 4.17

F1,30 at the 1% level = 7.56

Therefore, there is a significant difference in wet bulb temperatures at the inlet and exhaust side of the air treated bin. A constant total heat process did not occur. Evidently there was enough temperature differential between the room atmosphere and the bin contents to cause a significant amount of heat transfer through the plywood bin walls. same type of a statistical test applied to the two sets of wet bulb temperatures in the ozone treated bin shows that the difference is highly significant or significant at the one percent level. These two tests indicate that more heat transfer must have occurred through the bin walls of the ozone treated bin and into the material being dried. The extra heat supplied by such a transfer could be partly responsible for a slightly greater rate of moisture loss in the ozone treated bin. To prevent such interference from unequal quantities of heat transfer the bin walls would have to be so constructed that they have a higher resistance to heat flow. The amount of insulation required would have to be determined from the anticipated temperature differential and the type of insulation intended for such use.

Water vapor pressure differential is known to be a very important factor in drying. Therefore, the vapor pressures at the bottom or inlet of both the control and treated bins were compared by the same statistical procedure that was used for wet bulb temperatures. No significant difference was found as would be expected when both bins were supplied with air from the same source. The vapor pressures or absolute

humidities should not be different unless there is some element in the system that would cause a dehydration of the air or air-ozone mixture which flowed through the material being dried.

The last statistical test applied to the data of Corn Drying Test No. 1 compared the dry bulb temperatures at the inlet of the air and ozone treated bins. This test showed that there was a highly significant difference between the two groups of dry bulb temperatures, the higher average temperature occurring at the inlet to the ozone treated bin. Two factors may have been responsible for the slightly higher dry bulb temperature average at the inlet to the ozone treated bin. One of the factors definitely was the ozone generator which generated heat from the silent arc discharge, the heat being discharged with the air-ozone mixture into the centrifugal fan which supplied the ozone treated bin. Another factor may have been the difference in fan construction and the resulting work done on the air which may have caused some additional heat to be developed in the air-ozone mixture that supplied the ozone treated bin. The backward curved blade centrifugal fan supplied the ozone treated bin and a forward curved blade centrifugal fan supplied the air treated bin.

As an approximate check on the amount of moisture removed from the air and air-ozone treated bin, net weights of the corn being dried were checked at a number of time intervals.

Net weight losses are usually assumed to be moisture losses when a material is dried. This is an assumption which can be somewhat in error because there may be some loss of dry matter. However, any dry matter loss would be small except in cases where excessive heat is applied to the material being dried as might occur in an oven at a high temperature. In Figure 11 the net weight loss is shown with respect to time. It appears that the weight loss rate is very constant at the beginning of the drying time but decreased as the corn being dried began to approach a moisture equilibrium condition with the drying air or air-ozone mixture. There never was a net weight loss difference between the air and air-ozone treated bins which exceeded two pounds. The initial net weight (weight before drying) in each of the two bins was four hundred seventy-two pounds.

No accurate ozone concentration determinations were made during any drying tests because of difficulties with the chemical method of gas analysis. There were, however, positive indications that ozone was produced by the generator. For a detailed discussion of the problem involved in the determination of ozone concentrations see Appendix II.

In the first corn drying test the thermocouples located in kernels always indicated temperatures lower than that of the air beside the kernel when the grain at the level of the thermocouple was losing moisture. After the kernel which

	<u> </u>				,				.															_	- 39) —		•
										· · · · · · · · · · · · · · · · · · ·		!																
	-							ļ +	1	1	ļ	1																
								l: L:				i				11												
								i				<u> </u>				1									9			
			:																						=			
														l												:		
							1 : :		1	1								: : :			T				<u>4</u>			
												1:::	: .:					7							=			
	1																	2										
	1							:		ij	1					 		340		Ž								
										1						Ī		1	1	7					8	1		
									1	11	V							WEIGHT SOCIETION	3 (ON DRI ING	AIR INCALED	7			=			
										1	N			1				U	} (5								
				: : :					1		1,1		1	Ĭ.				Č				2						Ī.,
				- -						1	1,7	Ý					T	ŀ				n			8			
												1						Č		2		1			=			
										† -		1	1					N	9	5						9		
										1		† · · · ·	17.							•						-	1	_
													1,) 				1		ā ;					8	7		
														1		1 ::									Ø	ADJUSTED TIME		FIG.
								1						, ·												TED		L
															1,	//										20		
												1				1									0	0	. i	
									1								1							<u> </u>	Ø			
			::-			i iii			1			1					1	7										
																		1										
															-				1									
					111			 											1	% ::		1			4			
					-				-		1:								- :	1								
						-										 -			,		Z							
	: :			- : :					1	 -							1			†*** *	1	1			_	•		
				:						::-		<u> </u>										1			8			
	1									1	-					†	†					†:			 i			
				1									:; • .										1					
	†									1:																		
																				;:::					0	: :		\dashv
	1					 		Q	P			2	5 -						1.11	G	i			4	•	-:		
																S O	nud	d									-:- :	
1					1						1::::		::::1				11111	ī	:::: i	::::	11111	[

,

included the thermocouple assumed the same temperature as the surrounding gas that flowed past the grain at the same level, it would indicate that a moisture content close to equilibrium with the air or air-ozone mixture had been reached at that position in the bin. Because of this temperature characteristic within a kernel that was losing moisture more thermocouples were employed in all succeeding tests. It was reasoned that possibly the rate of drying in the bin and the end point of drying required could be correlated with temperature differentials between a particle of the material being dried and the surrounding drying medium. Figure 12 shows the positions of thermocouples in the second corn drying test and in both bean drying tests. Thermocouples 8 - 1 through 12 - 2 were placed in the air treated bin while thermocouples 12 - 3 through 12 - 12 were placed in the air-ozone treated bin. couples 8 - 1 and 12 - 3 were placed in the plenum chambers of the air treated and ozone treated bins respectively. Thermocouples 12 - 2 and 12 - 12 were placed in the gas flow at the exhaust side of the air and ozone treated bins respectively. All other even numbered thermocouples were placed in plexiglas shields next to a kernel or bean that contained a thermocouple designated by an odd number. The purpose of the plexiglas shields was to prevent thermocouple contact with a drying particle. These pairs of thermocouples were positioned at various levels in the two bins as shown in Figure 12. The tabular data in Appendix III includes the record of all these temperatures. However, upon inspection of the temperatures

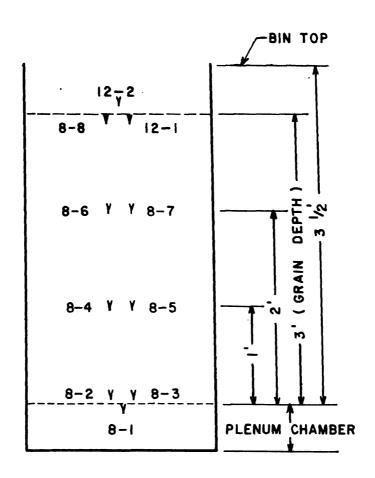


FIG. 12
THERMOCOUPLE (T.C.) LOCATIONS IN AIR
DRYING (CONTROL) BIN OF CORN TEST NO. 2,
also BEAN TESTS NO. 1 and NO. 2

NOTE: T.C.s in O₃ treated bin were in the same relative positions (8-1 compares with 12-3, 8-2 with 12-4, 8-3 with 12-5, etc.). 8-1 indicates that the 8 point recorder was registering that temperature on point NO.1.

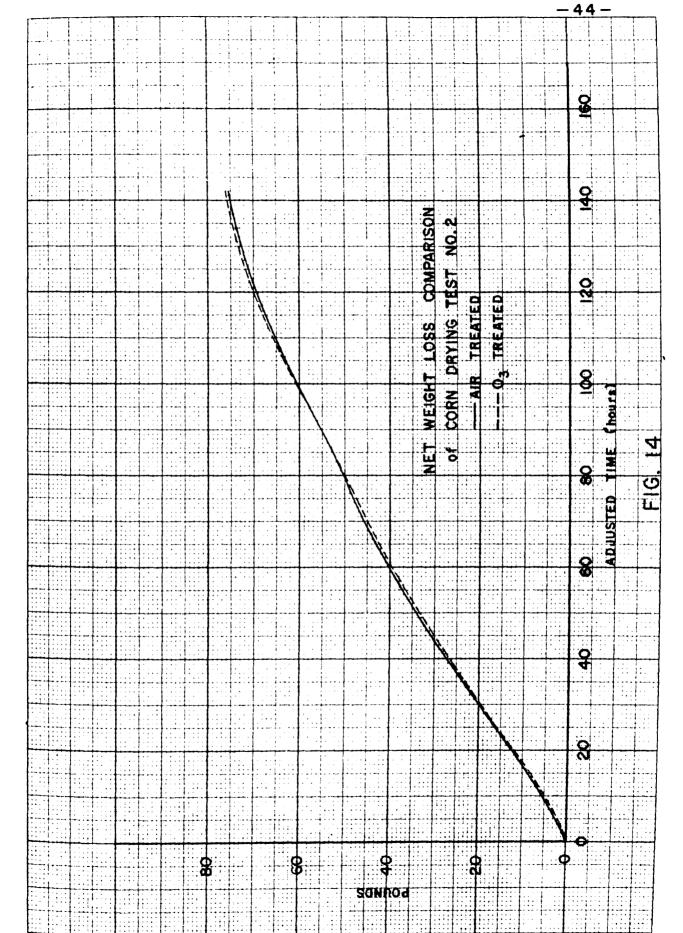
obtained it appeared that it would be quite difficult to apply such a method to determine the amount of drying that had taken place in any particular part of the bin. As a result moisture samples that were withdrawn at various time intervals were accepted as the most reliable method of determining moisture conditions in the bin.

Corn Drying Test No. 2 was conducted practically the same as the first corn test except that the six unit ozone generator variac was set at the maximum recommended voltage (115 volts on the primary of the transformer). A grain trier without partitions was employed in this test to obtain moisture samples from the bins. The difficulties in using the trier were explained in the section on apparatus. The mixing of the samples from different levels in the bin due to the position in which the trier had to be used produced some erratic drying rate curves as shown in Figure 13. Those results should be considered invalid.

However, it should be reiterated that the sampling technique with the trier was changed for the two bean tests and those moisture content determinations should not contain any great errors. In this case where the method of sampling was in error the Net Weight Loss Comparison of Corn Drying Test No. 2 (Figure 14) is of some value. Again the net weight loss rate is quite constant for the first part of the test but is retarded as most of the corn approached equilibrium

MADE IN U. S. A.

20 X 20 PER INCH



conditions. It should be noted that there is a very small net weight loss difference between the air and ozone treated bins. A statistical test to compare the wet bulb temperatures at the bottom of the air treated bin with those at the top shows no significant difference. The same is also true for the ozone treated bin. A comparison of water vapor pressures at the bottom of both bins shows that there is no significant difference as would be expected. However, a comparison of dry bulb temperatures at the inlet of both bins shows only a significant difference which is probably responsible for the slightly greater weight loss in the ozone treated bin. A change in the setting of the ozone generator apparently had no effect on the rate of moisture removal when the results of Corn Drying Test No. 1 and Corn Drying Test No. 2 are compared.

There appeared to be some bleaching action by the ozone in the corn of the treated bin. Corn oil is known to absorb ozone without decomposition of the ozone molecule. Some medical research has been done with ozonated corn oil [23].

Figure 15 shows the drying rates at four levels in the air and ozone treated bins of Bean Drying Test No. 1. In observing the curves it appears that moisture driven out of the bottom layers of material in the bin is absorbed farther up in the bin. That is undesirable because the same moisture must be driven out of the beans more than once. It is not yet known what depth and air flow rate is the most desirable

MADE IN U. S. A.

20 X 20 PER INCH

for white pea bean drying. Possibly a higher flow rate of air or a smaller depth of beans or both would be more advantageous. This remains to be determined by further work. layers at the bottom and one foot above the floor in the ozone treated bin apparently dried slightly faster while beans in the top half of the ozone treated bin were slightly retarded in losing moisture when compared with the control or air treated bin. Statistical analysis of the two sets of wet bulb temperatures in the air treated bin and also in the ozone treated bin showed no significant differences. In other words heat transfer through the bin walls in the first bean test are insignificant. Water vapor pressures at the bottom of both bins in this test were not significantly different, whereas the dry bulb temperatures had a difference that was significant at the one percent level. Figure 16 shows no difference in net weight loss in the control and test bin until the end of the drying process. The difference is then exceedingly small, there being a difference of only a pound in favor of the ozone treated bin. Such a small difference cannot be considered significant when almost six hundred pounds of wet beans were initially placed in the bins for the first bean test.

In the second bean test the ozone generator was set at the maximum recommended primary voltage (115 volts). Air and air-ozone flow was the same as in all previous tests, i.e. 4 c.f.m./bu. The drying rate curves for the various bin levels as shown in Figure 17 are practically identical to those of

SONNOL

48-

ADJUSTED TIME (hours

08

9

MADE IN U. S. A.

20 X 20 PER INCH

,

the first bean drying test. Wet bulb differences within both bins are again insignificant. Water vapor pressure differences at the bottom of both the control and test bin are also insignificantly different. In the case of this last test only, an insignificant difference occurred between the two groups of dry bulb temperatures, one group being taken from the plenum chamber of the air treated or control bin and the other group being taken from the plenum chamber of the ozone treated or test bin as usual. The temperature and initial humidity conditions of this last test on beans were most desirable in that there were no significant differences in the factors (except ozone) that are known to affect drying rates. The drying rate curves of this last test (Figure 17) indicate that ozone may have some affect on the rate of moisture removal but it appears to be small. When the fact is considered that this maximum output of a six unit ozone generator was supplying part of the gaseous mixture to a small volume of wet grain (approximately 9.6 bushels) it appears to be impractical to use ozone as a drying agent. The net weight loss comparison shown in Figure 18 again supports the conclusion. A net weight loss difference greater than two pounds never occurred in the second bean drying test.

Field Emergence and Laboratory Germination Tests

Beans were taken from the bottom layers of both the air and air-ozone treated bins of Bean Drying Test No. 2. All culls and foreign matter were picked out by hand to obtain clean beans. Four lots of one hundred seeds each were randomly taken from the air treated beans and four lots of one hundred seeds each were randomly taken from the air-ozone treated beans. These samples were planted in the field in four blocks. Each block contained one hundred of the control seeds and one hundred of the treated seeds. The two lots of seeds for each block were randomly selected and planted.

Figure 19 shows the four blocks of beans.

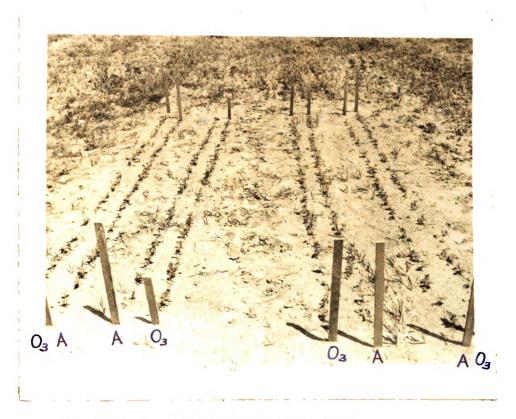


Figure 19 Field emergence test.

From left to right the blocks are numbered 2, 1, 3, and 4. The ozone treated and air treated rows are designated in the figure thus: A's are air treated and 03's are ozone treated. Germination conditions at the time of planting on May 27, 1952, were excellent. Eight days after planting emergence counts were made for all blocks. Each cotyledon that was above the soil surface was counted as one successful emergence. It is a general rule that good seed beans should emerge within a week or ten days after planting if conditions are favorable. The results of these counts are shown in Table II.

TABLE II

WHITE PEA BEAN EMERGENCE IN THE FIELD
EIGHT DAYS AFTER PLANTING

Treatment	1	2	3	4	Totals
03	44	47	40	35	166
Air	51	52	41	31	175
Totals	95	99	81	66	341

The analysis of this data is as shown in Table III.

TABLE III

ANALYSIS OF VARIANCE OF FIELD EMERGENCE TEST
FOR WHITE PEA BEANS

Source	d.f.	S.S.	M.S.	F
Total	7	436		-
Blocks	3	337	112.5	3.79
Treatment	1	10	10.0	0.34
Error	3	89	29.67	

Therefore, any difference due to treatment is not significant. Figure 20 shows the plants in the middle of block 2.



Figure 20 Comparison of plants in block 2.

The plants that developed from the ozone treated seeds are in the top row and those from the air treated are in the bottom row. There was no apparent difference in the vigor of the plants.

Beans taken from the same positions in the bins as for the field emergence tests were germinated in wet paper germinators. One hundred seeds were placed in each paper roll. The rolls with the seeds were placed in inverted jars in which a slight opening at the mouth was allowed for ventilation but where evaporation of moisture from the paper roll germinators was retarded. Five days after the seeds were placed in the germinator rolls the rolls were carefully opened and the seeds with strong sprouts were separated from the rest and counted. The number of vigorous germinations in each roll of one hundred seeds is given in Table IV.

TABLE IV
WHITE PEA BEAN GERMINATION IN THE LABORATORY

	Trea				
Replication	Air	Ozone	Totals		
1	39	62	101		
2	41	60	101		
3	47	37	84		
4	35	45	80		
5	46	52	98		
6	44	40	84		
Totals	252	296	548		

The statistical analysis of these results is shown in Table V.

TABLE V

ANALYSIS OF VARIANCE OF THE LABORATORY
GERMINATION TESTS OF WHITE PEA BEANS

Source	d.f.	S.S.	M.S.	F.
Total	11	804.66		
Replications	5	233.67	46.73	
Treatment	1	161.34	161.34	2.61
Error	5	309.65	61.93	

 $F_{1.5}$ at the 5% level = 6.61

Therefore, there is no significant effect on germination, even though the maximum output of the six unit generator was applied to these beans which were taken from a position next to the inlet of the bin. Figures 21 and 22 show the germinated beans in the laboratory.

It was noted in the laboratory germination tests that the air-ozone treated beans supported a somewhat smaller amount of mold growth than the air treated in some of the germination rolls. No attempt was made to get any mold data because that was not one of the objectives of the experiment.

Ozone could possibly be very useful as a fungicide for beans, especially in the packaging of beans that have a moisture content over that which is now accepted as an allowable maximum



Figure 21 Laboratory germinated beans - air treated.



Figure 22 Laboratory germinated beans - ozone treated.

CONCLUSIONS

- 1. Ozone does not appreciably influence the removal of excess moisture from shelled yellow dent corn or white pea beans.
- 2. Ozone, in the concentration supplied by the six unit generator, produced no significant effect on the germination quality of white pea beans in the field or in the laboratory.
- 3. The edible quality of white pea beans appears to be unchanged by exposure to ozonated air.
- 4. Ozone may have a definite value as a fungicide providing high enough concentrations are employed. This remains to be determined in a later project.
- 5. The technique for the accurate determination of ozone concentrations will have to be further developed. Some means more rapid than the chemical method would be highly desirable.
- 6. The optimum depth, temperature, and air flow rate for drying white pea beans still remains to be determined.

APPENDIX I

Thin Plate Orifice Characteristics

Severns and Degler [19] present the following equation for flow through a thin plate orifice.

Q = 0.526 C D^2 $\sqrt{\frac{p}{da}}$ c.f.s. at exit pressure and entrance temperature

when

C = coeff. of discharge

D = orifice diameter in inches

p = pressure differential in p.s.i.

 $d_a = density of air in pounds per foot³ at exit pressure and entrance temperature.$

Both C and the downstream vena contracta tap locations for various diameter ratios are given in curve forms in reference [19]. Considering the 3 inch orifice and 6 inch pipe, which was used in this experiment, a 0.5 diameter ratio is found on the graph and the corresponding C and vena contracta tap (downstream tap) location is read. The value of C is 0.628 and the downstream tap location os 0.63 of the 6 inch pipe diameter. The upstream tap is always placed one pipe diameter above the orifice place for this size of pipe.

Length requirements for straight, smooth pipe, both above and downstream from orifice plates to insure a correct type

of flow, are given in the reference.

In the equation Q is a known value as it is determined from either the cross sectional area of the bin floor in terms of c.f.m. per square foot or from the volume of the stored grain in terms of c.f.m. per bushel. C and D are fixed values when the orifice and pipe size is chosen. The density of air (d_a) can be calculated for prevailing conditions by $W = \frac{PV}{RT}$. By the general gas law the amount of standard air desired can be converted to volume Q at prevailing conditions. The only unknown is the differential pressure (p) in p.s.i. which must be calculated to determine its equivalent in inches of water in which the manometer is calibrated.

Example: What differential pressure in inches of water is required to force 4 c.f.m. per bushel through 10 bushels of grain when a 3 inch orifice is used in a 6 inch pipe? Room temperature is 70° F. and the barometric pressure is 14.3 p.s.i.a.

4 c.f.m./bu. x 10 bu. = 40 c.f.m. require of standard air. (air at 70° F. and 14.7 p.s.i.a. is standard)

$$\frac{P_1 \ V_1}{T_1} = \frac{P \ \text{std. V std.}}{T \ \text{std.}}$$

$$V_1 = \frac{P \ \text{std. V std. T}_1}{P_1 \ T \ \text{std.}} \text{ and Tl} = T \ \text{std.}$$

$$V_1$$
 or $Q = \frac{(1/4)(14.7)(40)}{(1/4)(14.3)} = 41.2$ c.f.m. at room conditions

$$P_1 V = W R T_1$$

$$W = \frac{P_1}{R} \frac{V}{T_1}$$

$$d_a \text{ or } W = \frac{144}{53.3} \frac{(14.3)}{(530)} = 0.0728 \text{ lb./ft.}^3$$

$$Q = 60 (0.526) \text{ C } D^2 \sqrt{\frac{p}{d_a}} \text{ c.f.m.}$$

$$p = \frac{Q^2}{(60)^2} \frac{d_a}{(0.526)^2} \frac{(0.526)^2}{(0.526)^2} \frac{(0.628)^2}{(0.628)^2} \frac{(3)^4}{(3)^4} = 0.00388 \text{ p.s.i.}$$

$$1 \text{ inch of water} = 0.0361 \text{ p.s.i.}$$

$$\frac{x \text{ in.}}{1 \text{ in.}} = \frac{0.00388}{0.0361} \frac{\text{p.s.i.}}{\text{p.s.i.}}$$

$$x \text{ inches of water} = \frac{0.00388}{0.0361} = 0.1075$$

Therefore, the manometer must read 0.1075 inches of water in differential pressure for the orifice to deliver 40 c.f.m. of standard air at the conditions given. It should be noted that the exit pressure was always assumed as being equal to the barometric pressure in this experiment because static downstream pressures when added to the barometric changed the absolute pressure only in the magnitude of a few thousandths of a p.s.i.a. This accuracy cannot be obtained in slide rule calculations which were used.

The following set of curves was used with the three inch orifice plate in a six inch pipe to control air and air-ozone flow through the bins. The short curves which cut across the long curves are equal air weight lines. This is a convenient means of referring all flows to standard conditions.

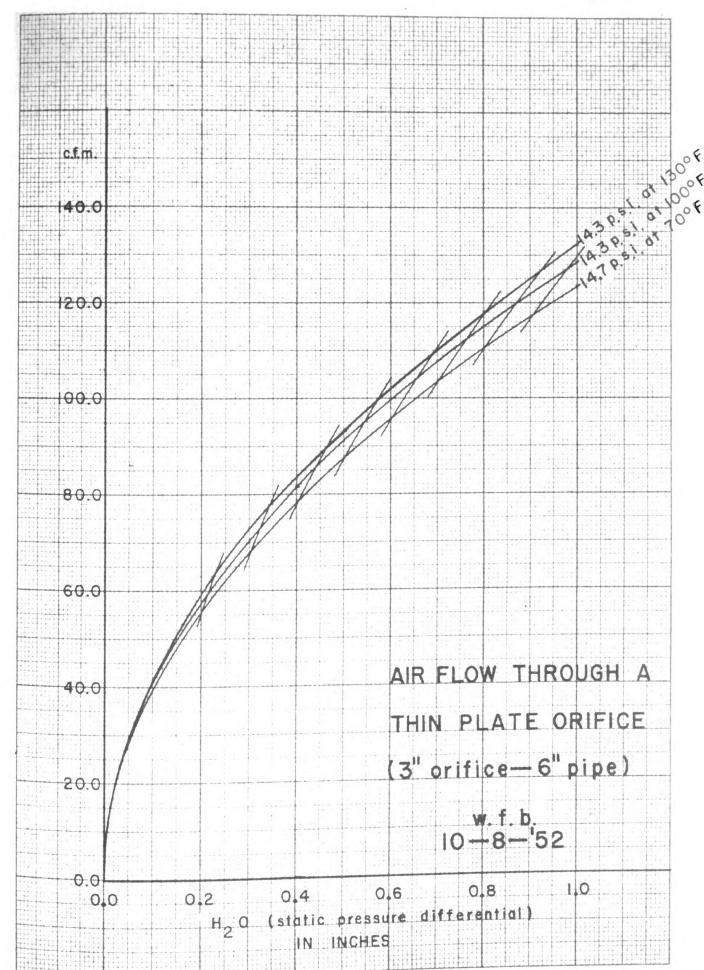


Figure 23 Air flow through a thin plate orifice.

APPENDIX II

Ozone Concentration Determination

All literature investigated by the author late in 1951 and early in 1952 indicated that the potassium iodide-starch method had been used for some time and was considered the most reliable. However, more recent information [23] shows that a change in technique employed in the potassium iodide-starch method is necessary to obtain valid results. A discussion of the problems encountered in using the old method and the recent information obtained follows.

Schomer and McColloch [18] worked with ozone in apple storage and are the authors of a U.S.D.A. (January 1948) circular which describes in quite some detail the procedure they followed in determining the concentration of ozone. It would be best to quote many of the details of the procedure so that a clearer understanding of the problem may be had. According to Schomer and McColloch who followed Thorp's modified starch-iodide method (Industrial and Engineering Chemistry. 12:209. Analytical ed.,) the following solutions are needed:

2 normal potassium iodide

buffer solution (5 g. Al $Cl_3 \cdot 6 H_2O) + 1$ g. NH_4Cl made up to 1 liter with distilled water)

0.01 normal sodium thiosulfate

starch solution as an indicator

Schomer and McColloch give a procedure as follows:

To 100 ml. of 2 N KI solution was added 5 ml. of buffer solution and 100 ml. of the solution was placed in the gas wash bottle. The gas was drawn through until a yellow color was obtained. The volume of air was accurately read from the gas meter and the free iodine that was liberated was titrated with a 0.01 N solution of sodium thiosulfate; starch solution was used as the indicator. An equal volume of air free from ozone drawn through a second washing bottle of K I solution constituted the check. The difference in the titration values was used for determining the ozone concentration in parts per million. Since 1 ml. of 0.01 N solution of sodium thiosulfate equals 0.112 ml. of ozone the formula

 $\frac{T \times 112}{s}$ = parts per million of ozone by volume

where T = ml. of sodium thiosulfate required for titration and S = liters of gas sample used in analysis after correction to standard conditions.

M. B. Jacobs [14] also refers to Thorp's publication (Industrial and Engineering Chemistry, 12:209. Analytical ed., 1940) and makes the following statements:

Ozone is usually estimated quantitatively by passing the gas through a neutral solution or better through an alkaline solution of KI, acidifying the solution with sulphuric acid (dilute), and titrating the free iodine with O.Cl N sodium thiosulfate solution. This method is specific only in the absence of certain oxidizing agents. The greatest sensitivity that can be obtained with this method is the detection of 0.0013 mg. of ozone per ml. of 2 N KI solution.

Air containing as little as 0.1 p.p.m. by weight of ozone must commonly be analyzed. This concentration requires that 10 liters of air be passed through each ml. of KI test solution before any ozone can be detected by the above method.

Thorp increases the sensitivity of the KI method by the addition of a buffer solution consisting of 5 g. of Al Cl₃ · 6 $\rm H_2O$, and 1 g. of NH₄ Cl made up to one liter. Five ml. of this solution is added to each 100 ml. of KI test solution before the test is made. The solution should not be acidified during the titration. The use of Al Cl₃ · 6 $\rm H_2O$ as outlined gives a minimum sensitivity of 0.00062 mg. of ozone per ml. of KI. The KI solution so treated will have a stability of

over 3 hours, which allows sufficient time for ordinary analysis. Exclusion of light from the solution will greatly increase stability, as will the use of brown bottles.

No cork or rubber should be used in contact with ozone. Not only does the ozone destroy these substances, but they will seriously affect the accuracy of the determination. Ground glass connections are preferable, but neoprene or rubber and cork coated heavily with shellac or lacquer may be used.

Only ultra violet light will produce pure ozone. An ozonizer that uses sparks of any kind will produce pure impurities in the form of oxides of hydrogen and nitrogen. KI will, of course, liberate free iodine in the presence of these gases. Thorp states that he has found oxide impurities as high as 75% of the total yield. To make sure that only pure ozone reaches the absorbtion bottle containing KI solution, place a scrubbing tube containing chromic acid and a tube containing potassium permanganate in the train before the KI absorber.

Draw the ozone sample through 100 ml. gas washing bottles fitted with a glass disc disperser until a definite deep iodine color is noticed in the first bottle. Titrate with 0.01 N sodium thiosulfate solution standardized against resublimed iodine, using a 2 - 3 ml. microburette. For ozone concentrations of less than 0.5 P.P.M., the gas washing bottles should be of the semi-micro type and the test solution should not exceed 10 ml.

Jacobs also states that the usual rate of gas sampling is 0.5 to 1 liter per minute and coarse dispersers in the gas wash bottles are usually preferred. With such information and much assistance from the Department of Agricultural Chemistry the required pyrex ware and reagents were obtained. The chemical equipment was assembled and many samples of air-ozone mixtures and air samples for checks were run through the absorption system. Titration results never seemed to run consistently so the technique of sampling and titration were thoroughly discussed with Dr. Benne of Agricultural Chemistry.

No serious faults could be found in the manipulation of the

apparatus so a careful restudy of reference material was made.

Two statements in Treadwell and Hall [24] were noted which

read as follows:

It makes a difference, however, whether the ozone reacts with a neutral or with an acid solution of KI. In the latter case far too much iodine is liberated, although in the former case exactly the right amount is set free.

The two above statements agree with one of the statements by Jacobs concerning the pH of the KI solution. Jacobs stated that the gas should be passed through a neutral solution or better through an alkaline solution. It was therefore decided to check pH values of the KI solution without any buffer added and also with varying quantities of buffer solution added. One hundred ml. of unbuffered solution were taken and increments of buffer were added until the 5 ml. maximum was used as directed in the references. The results of the pH test ran as shown on the following page, Table VI.

TABLE VI

PH CHANGE OF POTASSIUM IODIDE WITH BUFFER ADDITIONS

					Solı	utio:	n	рН
100	ml.	of "	ΚI			ml.	buffer	8.81 8.48
11	17	11	11		0.10	11	tt	
11	11	ŧŤ	11		0.20	11	11	7.72 7.14
11	11	11	††		0.40	11	11	6.70
11	11	11	11		0.50	11	11	6.43
11	ft	11	11		0.60	**	11	6.18
11	11	11	11		0.70	11	11	6.00
tt	11	11	11		0.80	11	11	5.83
71	11	11	11		0.90	11	***	5.63
11	11	31	11		1.00	11	**	5.63 5.43
11	11	rt	11		1.25	tt	11	5.08 4.91
***	11	11	11	+	1.50	11	**	4.91
11	11	11	11	+	1.75	11	11	4.80
11	11	11	11		2.00	11	11	4.72
**	11	11	***		3.00	!!	**	4.72 4.55 4.46
11	11	11	11	+	4.00	!!	11	4.46
11	11	11	11	+	5.00	11	† †	4.39

The above results definitely prove that there is a contradiction within the reference by Jacobs [14]. It was then decided to eliminate the addition of buffer entirely and observe the results. Titration values still did not appear to be consistent. However, it should be noted that a short time after the experimental drying was concluded an article in the April 17, 1952, issue of Analytical Chemistry appeared on the subject of buffer solution addition to potassium iodide in the analysis of ozone-oxygen mixtures. Birdsall, Jenkins, and

Spadinger [5] wrote a preface as follows:

A survey of the literature on ozone for the past 50 years discloses many contradictory and confusing statements concerning methods of ozone determination. This work was undertaken to clarify the situation and establish a reliable method. A chemical method is described, which proved suitable for ozone-oxygen mixtures containing up to 25% ozone. A physical method has been devised for use as a standard of comparison in testing this chemical method. Comparisons have been made with other chemical analytical methods for ozone. This work should clarify the present unsatisfactory situation regarding the chemical analysis of ozone-oxygen mixtures. As the uses of ozone increase, these methods should be of increasing importance.

In the conclusion of the same article the following statements were made:

In the concentration range investigated (1 to 25 mole %) the use of 2% unbuffered aqueous solution of potassium iodide for the analytical determination of ozone gives precise results which are accurate to 2% when compared with a physical method. The use of boric acid as a buffer is unnecessary and can lead to erroneous results.

The statement is also made in the above article that it is the low pH which brings about the erroneously high results. As was previously stated, the elimination of the buffer did not prove to be the entire solution to the difficulty in the gas analysis. When running relatively pure air (air free of any ozone) through the absorption system a stable titration correction factor still could not be obtained. It was observed that there was some carry-over of the contents of the potassium permanganate wash bottle into the potassium iodide wash bottle. Just a small amount of this carry-over seemed to take place; therefore, it was not very apparent and some

time passed before it was noticed. This action took place with a gas flow rate of about 300 cc. per minute, even though 0.5 to 1 liter per minute is recommended as mentioned in a previous reference. The solution to this problem seemed quite obvious. The sequence of units in the absorption system in which the carry-over took place was as follows: the gas sample passed from the bin through the flowmeter, through the scrubbing tube containing a dry chromium compound (Cr₂O₃), through the tube containing a solution of potassium permanganate, and thence through the ozone absorbing tube or potassium iodide wash bottle. two scrubbing units before the ozone absorption bottle were used for the elimination of the gaseous impurities in the ozone-air mixture; namely, the oxides of nitrogen and hydrogen which are produced in any electrical discharge ozone generator. The impurities must be removed before the gas sample reaches the potassium iodide solution or serious errors could result due to the amount of iodine freed in the potassium iodide solution. To prevent any further carry-over into the ozone absorbing solution it seemed that the most logical thing to do was switch the positions of the two scrubbing tubes that removed impurities in the gas sample. revised arrangement put the dry reagent (Cr₂0₃) just before the ozone absorbing wash bottle. A small filter of pyrex wool was placed in the tube connection between the dry reagent scrubbing tube and the ozone absorbing wash bottle to trap any of the dry, fine Cr_2O_3 that could be picked up by the

flowing gas sample.

Following the change in the sequence of the absorption system a radical change in titration values occurred. tremely low net titration values were obtained which seemed to run more consistently. This led to the belief that possibly the ozone generator was not producing ozone in any quantity at all. However, it was finally learned that one of the scrubbing tubes to remove impurities contained the wrong reagent. This may have been due to confusion which is quite often the case when one particular compound is identified by more than one name. Personal correspondence with Foster D. Snell, Inc. in New York advised the use of one scrubbing tube of chromium trioxide and one scrubbing tube of potassium permanganate ahead of the potassium iodide washing bottles. Jacobs [14], who was quoted previously, stated that a scrubbing tube containing chromic acid and a tube containing potassium permanganate should be placed in the train before the potassium iodide absorber. It is believed that the term chromium trioxide may be responsible for such a mistake. Cr2O3 (chromic oxide) has three atoms of oxygen and was probably confused with Cr O3 (chromium trioxide) which also has three oxygen atoms. Chromium trioxide is the compound that should have been obtained because it is the anhydride of chromic acid.

At the time this mistake just discussed had been found all four of the drying tests had been concluded. However, the proper reagents, according to the references, were placed in the wash bottles and gas samples were taken directly from the samples were taken directly fr

discharge of the ozone generator, the variac being set on 115 volts which was the maximum recommended primary voltage. All samples were drawn at the rate of about 300 cc. per minute for a duration of one-half hour each time. The first sample was taken through the potassium iodide wash bottle only, thus allowing any oxides of nitrogen and hydrogen to release iodine also. The net titration value for this case was 6.88 cc. The next sample was taken through only two wash bottles, the one which contained potassium permanganate and the second which contained the potassium iodide. net titration result of this test was 5.60 cc. of 0.01 N sodium thiosulfate. The third test contained all the scrubbing tubes or wash bottles as recommended. This procedure indicated that the two scrubbing tubes, the purpose of which was to remove impurities, both removed constituents of the gaseous mixture that could liberate iodine from the potassium iodide solution. The result of the last test would indicate that the ozone generator used to supply the test bin did produce ozone in reasonable quantity, roughly 45 P.P.M. by volume directly from the generator exhaust. Observation of another incident indicates that ozone definitely must have been present during the drying test. At one time during a gas sampling test at the door to the plenum chamber of the test (or ozone treated) bin a rubber band under tension due to holding a pyrex tube connection together was observed to pull apart very rapidly. The rubber band was in a direct path of the air-ozone

mixture which was escaping from the partly open door to the plenum chamber. Natural rubber under tension is known to fail quite rapidly when subjected to relatively low ozone concentrations (concentrations of a few parts per million).

Recent correspondence and consultation with Dr. Clark E. Thorp of the Armour Research Foundation who has done much work with ozone believes that the technique of ozone determination by the potassium iodide-starch method as given in several references must be changed. The previous method which employs scrubbing tubes before the potassium iodide wash bottle(s) introduces appreciable error in the determination of ozone. The impurity scrubbing tubes remove not only the oxides of nitrogen and hydrogen but also some of the ozone, which action is undesirable. Thorp stated that it is best to run a total analysis, that is, determine the titration value for the ozone plus the impurities and then make a separate analysis of the impurities, subtract the results of the impurity test from the total, and thus determine the value for the ozone. The aluminum and ammonium chloride buffer (which was originally suggested by Thorp) described in the references should be used to prevent the potassium iodide solution from becoming alkaline during the test because such a condition can result in error. Thorp also discourages the use of fritted glass disc dispersers because he believes that a surface of that type is responsible for some breakdown of ozone when it makes contact as it flows through. Thorp used standard Allihn bottles for the buffered

potassium iodide solution when he obtained data on the influence of temperature on ozonizer efficiency and also on another project in which the influence of water vapor on ozonizer efficiency was determined.

In the case where an ozonizer properly constructed is supplied with a very dry air, a negligible amount of impurities are produced. Proper construction is understood to mean that the electrodes and dielectric of the generating elements are made so that no arcing can occur but only a silent ultra-violet discharge takes place. Supplying the generator with 100% 02 will eliminate any possibility of impurities being produced. Some laboratory generators have been made by modifying a Liebig apparatus and producing ozone from oxygen that was forced through from a tank. From the standpoint of laboratory usage and the usual scale of experimental work, which is in most cases on a small basis, a modified Liebig apparatus supplied with pure oxygen is very often satisfactory. The voltage (secondary) supplied to this apparatus may be varied in the general range of five thousand to fifteen thousand volts. The products of this apparatus when supplied with only oxygen are oxygen and ozone. result simplifies the chemical analysis of the gas mixture because of the fact that no impurities are produced. Therefore, only bottles containing one reagent, the buffered potassium iodide, are necessary. If a larger amount of ozone must be produced several of the above described units can be

mounted in parallel on the high voltage secondary of the transformer.

Thorp found that as the operating temperature of the ozone generator is decreased the output of ozone increased linearly when the secondary power was held constant. In other words an ozone generator should be run at as low a temperature as is possible from the economic aspect of refrigeration required. The humidity of air introduced into generators is also very important. Absolute humidity, not relative humidity, is the important factor in ozone production. When the absolute humidity becomes greater than 0.001 gram of water per gram of air or about 7 grains of water per pound of air there is a rapid decrease in ozone production. Absolute humidities less than this cause an insignificant change in the output of ozone generators. Therefore, when maximum output of a generator is desired it should be kept as cold as possible and when ozone is generated from air it must be dried as much as possible.

As yet there is no published procedure for the determination of ozone by Thorp's latest method. In personal correspondence he recommended the elimination of all scrubbing solutions with a direct analysis for the total of ozone and oxides of nitrogen. The oxides of nitrogen can then be determined separately by standard colorimetric techniques and the quantity of ozone determined by subtracting the determined amount of nitrogen oxides. The nitrogen oxide analysis would be unnecessary when pure oxygen is used.

APPENDIX III

Tabulated Temperature, Moisture and Weight Data for All Drying Tests

		TEMP.	GROSS	NET	NET	
DATIN			BIN	CORN	WEIGHT	
	ОТТОМ	TOP	WEIGHT	WEIGHT	LOSS	
	r. c. 2)	(T.C. #3)	(pounds)	(pounds)	(pounds	
3-13			588	472	0	
0 0	46 1/2°F.	42 °F.	585	469	3	
3-14	54	36	579 1/2	463 1/2	8 1/2	
11 11	58 1/2	37	575	459	13	
11 (59 1/2	36 ½	570	454	18	
3-1	59	34 1/2	566	451	21	
11 1	60	33 1/2	558	444	28	
0 1	60 1/2	34	552	438	34	
3-1	59 1/2	31 1/2	544	431	41	
0 1	61	31 1/2	539	426	46	
11 1	60 1/2	33	534 1/2	422 1/2	49 1	
3-1	61	32	527	415	57	
11 (64 1/2	32	521	409	63	
3-1	63 1/2	35	512 1/2	401 1/2	70 1/	
11	60	40	509 1/2	399 1/2	72 1/2	
3-1	62	55	507 1/2	397 1/2	74 1/2	
11 (62	57	505 1/2	397 1/2	74 1/2	

		TEMP.	GROSS	NET	NET
DA		BIN	BIN	CORN	WEIGHT
	ОТТОМ	TOP	WEIGHT	WEIGHT	LOSS
	r. c. # 6)	(T.C. #7)	(pounds)	(pounds)	(pounds
3-1	3		588	472	0
11	17 1/2 °F.	43 1/2°F.	585	469	3
3-1	455 1/2	37 1/2	579 1/2	463 1/2	8 1/2
11	4 6 0	38 1/2	574	458	14
11	62 1/2	38	569 1/2	453 1/2	18 1/2
3-	1162	35 1/2	565 1/2	450 V2	21 1/2
11	63	35	557 1/2	443 1/2	28 1/2
н	63	35	550 1/2	436 1/2	35 1/2
3-	162 1/2	3 3	543	430	42
п	163 1/2	33	538	425	47
н	64	34 1/2	5 3 3	421	51
3-	164	33 1/2	525	413	59
ш	67 1/2	33	519 1/2	407 1/2	64 1/2
3-	167	37 1/2	511	400	72
11	6.5	48	508	398	74
3-1	66	60 1/2	506	396	76
11	65 1/2	62	504 1/2	396	76

DAT	TOP			
			%	WATER
			RELATIVE	
		(psych.)	HUMIDITY	PRESSURE
3-28		F.		p.s.
3-29	55	53	88	0.19
0 0	56 1/2	54 1/2	89	0.20
3-30	55	53 1/2	91	0.19/2
3-31-	57 1/2	55 1/2	90	0.21 /2
11 11	61 1/2	60	92	0.25
4-1-	60	58	90	0.23
24 31	56 1/2	55	92	0.20 1/2
4-2-	52 1/2	51	90	0.17 1/2
0 0	53	51 1/2	90	0.18
4-3-	57	51 1/2	70	0.16
11 11	56 1/2	51	68	0.15 1/2
A	56.5	54.0		0.195
	3-28 3-29 " " 3-30 3-31 " " 4-1- " " 4-2- " " 4-3-	TEMP. (psych.) 3-28—°F. 3-29 55 " " 56 ½ 3-30 55 3-31 57 ½ " " 61 ½ 4-1-60 " " 56 ½ 4-2-52 ½ " " 53 4-3-57 " " 56 ½	DRY BULB WET BULB TEMP. (psych.) 3-28 — °F. — °F. 3-29 55 53 " " 56 ½ 54 ½ 3-30 55 53 ½ 3-31 57 ½ 55 ½ " " 61 ½ 60 4-1-60 58 " " 56 ½ 55 4-2-52 ½ 51 " " 53 51 ½ 4-3-57 51 ½ " " 56 ½ 51	DRY BULB WET BULB 7 ELATIVE (psych.) TEMP. (psych.) HUMIDITY 3-28 — F. — F. — F. — F. — S. — S.

quare SS both

1	DA TOP)		
1	DRY B	ULB WET BUL	-1	WATER
L	(psyc	h.) (psych.	- 1	TYPRESSUR
1	3-2	°F. — °F	-	p.s
	3-2 57	54 1/2	85	0.19 1/2
	58	56 1/2	92	0.21 1/2
3	-3 57	55 1/2	92	0.21
3	-3 59 1/2	57	86	0.21 1/2
"	63	61	90	0.25 1/2
4-	- 61	59	90	0.23 1
*1	57 1/2	55 1/2	90	0.20 4
4-	2 55 1/2	52 1/2	82	0.18
"	54 1/2	53	91	0.19
4 –	61 1/2	53 1/2	60	0.16
-	57 1/2	52 1/2	72	0.17
1	58.4	55.5		0,203

both

	F								_	=
	D	ATTOR)					_	_	_
		DRY B	ULB		BULB MP.	RELAT		WA		
		(psyc	h.)	(psy		HUMIC	YTIC	PRES	SSL	JRE
	4-	6-	°F.	_	−°F.	_	_	_	-	p.s.
	4-	7 45		42		79		0,1	1	1/2
	11	53 !	/2	51		83	1/2	0.1	7	
1	11 1	56		53		83		0.18 1/2		1/2
1	4-8	-8 53 1/2		51	1/2	87/2		0.17 1/2		1/2
L	" " 55			53		82 1/2		0.1	8	1/2
	4-9 54 1/2		2	51 /2 8		82	82 /2		7	
L	to 10	59		56		83		0.2		
1	4-10	56 1/2	2	53		80		0.1	8	
1		52 1/2		50		84		0.1	6	1/2
4	-11	51		48		82		0.15		
##	11	53 1/2		50 1/2		82		0.1	6	1/2
4-	-12	58		52!	/2	70		0.10	6	1/2
4	13 6	64		56		62	(0.1	8	
4 —	14 6	14 64		53		471/2		0.14		
-	15 63		!	511/2		45 (0.13		
4	5	6.0	5	1.5			C	. 16	65	5
	1									

square SS both ed

D

4-

4-

#-#-4.

4.

4

. :Ua:

S ed

F-						=
DA	TOP DRY BUI TEMP. (psych.	- 1	P. RELA		WAT	OR
4-6	0) (psych	.) HUMI	DITT	PRESS	
4-7		43	80		0.12	p.s
11 11	54	51 1/2		-	0.17	_
21 22	56 1/2	54	85		0.19	
4-8-	55	52	82		0.17	
" "	57	54 1/2	85		0,19	42
4-9	56	52 1/2	80		0.17	1/2
11 11	60	57	83		0.21	
4-10	57 1/2	55	86	(0.20	
" "	53 1/2	51 1/2	87	1/2 (0.17	42
4-11	52	49 1/2	84		0.16	_
" " 5	4 1/2	52	85	C	0.18	
	7 1/2	54	80	C	.18	42
4-17 6	5	57	62		. 19	
	5 1/2	54 42	49	0	. 15	
1-11 65	5	52 1/2	42	0	.13	_
57	.0	52.7		0	. 174	1

uare S both

d

		B WET B				WA	
	ych.	(psych	1.)	RELA		PRES	
4-16-	- °F		°F.	_	_		p.:
" " 59		56		83		0.20	-
4-17-58		55		84		0.19	1
" " 63		59		80		0.22	-
4-18 63		59 1/2	2	82		0.23	3
" " 66		62 1/2	2	82	1/2	0.26	6
4-19-60	/2	57 1/2		84		0.22	2
" " 64		60 1/2		82	1/2	0.24	7
4-20 63		60		85		0.24	1
" " 67		64		85		0.28	3
4-21-64		61		85	(0.25	5
" " 68 1/2	2 6	54 1/2		81	(0.28	3
4-22 72	6	4		65	(0.25)
4-23 71	6	0 1/2	1	55	(0.20	1/
" " 63 1/2	5	1 1/2	4	124	2 0	0.12	1/2
и и	_		_				
A 64.5	59	7			0	,22	9

square PSS both

DATTOP		- 1	T
DRY BU	LB WET BUL		WATER
) (psych.) HUMIDITY	
4-16	F. — °	F. —	p.s.i.
" " 59 1/2		83	0.21
4-1759	56	83	0.20 1/2
" " 63 1/2	60	82 1/2	0.23 1/2
4-1864 1/2	60	78	0.23
" " 66 1/2	63	82 1/2	0.26 1/2
4-19 63	59	80	0.22 1/2
" " 64 1/2	61 1/2	85	0.25 1/2
4-2064	61	85	0.25
" " 68	65	85	0.29
4-21-65 1/2	62	82 1/2	0.25 1/2
" " 70	66	80	0.29
4-22 73 1/2	66	67/2	0.27 /2
4-23 72 1/2	61 /2	53	0.21
" " 66	53	41	0.13
" "			
A 65.7 6	8.03	C	0.236
-			

re both

LITERATURE CITED

- Anon.

 American Society of Heating and Ventilating Engineers

 Guide. ed. 6, American Society of Heating and Ventilation Engineers, New York, 1928, pp. 329-336.
- Vapor Pressures in Studying Moisture Transfer Problems.

 Agricultural Engineering Journal. 19: 247-249. 1938.
- 3. Barre, H. J., and Kelly, C. F.
 Some Engineering Phases of Grain Storage. Agricultural
 Engineering Journal. 23: 79-82, 84. 1942.
- 4. Barre, H. J., and Sammet, L. L. Chapter 17, Storage of Grains. Farm Structures. New York, John Wiley & Sons, Inc., 1950.
- 5. Birdsall, C. M., Jenkins, A. C., and Spadinger, Edward. Iodometric Determination of Ozone. Analytical Chemistry. Vol. 24, No. 4. April 17, 1952.
- School Claydon, E. C.
 Grain Drying. <u>Electrical Review</u>. 144: 1081-1082.
 June 1949.
- 7. Ewell, A. W.
 Ozone and Its Application in Food Preservation. Refrigeration Engineering. 58: 1-4. September, 1950.
- 8. Ewell, A. W.
 Recent Ozone Investigations. <u>Journal of Applied Physics</u>.
 17: 908-911. November, 1946.
- 9. Ewell, A. W.

 Present Use and Future Prospects of Ozone in Food

 Storage. U. S. Egg and Poultry Magazine. 44: 302-303.

 May 1938.
- 10. Fenton, F. C.
 Storage of Grain Sorghums. Agricultural Engineering
 Journal. 22: 185-188. May 1941.
 - Homan, C. Effects of Ionized Air and Ozone on Plants. Plant Physiology. 12: 957-978. October 1937.

- 12. Hukill, W. V.

 Types and Performance of Farm Grain Driers. Agricultural

 Engineering Journal. 29: 53-54, 59. February 1948.
- 13. Huntington, E.

 Climatic Pulsations and an Ozone Hypothesis of Libraries and History. Conservation of Renewable Natural Resourses.

 Philadelphia, Univ. of Fenn. Press. pp. 125-131. 1941.
- 14. Jacobs, M. B.

 The Analytical Chemistry of Industrial Poisons, Hazards ed. 2. New York, Interscience Publishers, Inc. pp. 369-371. 1949.
- 15. Kelly, C. F.
 Research Work in Wheat Storage. Agricultural Engineering
 Journal. 21: 473-476. December 1940.
- 16. McCord, C. P., and Witheridge, W. N.
 Odors. ed. 1. New York, London, Toronto, McGraw Hill
 Book Co., Inc. pp. 181-183, 194-197. 1949.
- 17. Quisenberry, K. S.

 Grain Values to be Safeguarded During Conditioning and Storage. Agricultural Engineering Journal. 30: 586-588. December 1949.
- 18. Schomer, H. A., and McColloch, L. P.
 Ozone in Relation to Storage of Apples. U.S.D.A.
 Circular No. 765. pp. 1-24. 1948.
- 19. Severns, W. H., and Degler, H. E.

 Steam, Air, and Gas Power. ed. 4. New York, John Wiley

 Sons, Inc. pp. 399-401. 1948.
- 20. Shier, G. R., Miller, R. C., and Junnila, W. A.
 Forced Ventilation of High Moisture Grains. Agricultural
 Engineering Journal. 24: 381-382. November 1943.
- 21. Stahl, Benton M.
 Engineering Data on Grain Storage. Agricultural Engineering Data 1. (A.E. Index 11.732). St. Joseph, Michigan, American Society of Agricultural Engineers. May 1948.
- 22. Thorp, C. E.

 The Toxicity of Ozone. <u>Industrial Medicine and Surgery</u>.

 19: 2, 49-57. February 1950.
- 23. Thorp, C. E. Written and oral communication. October November 195

24. Treadwell, F. P., and Hall, W. T.

Analytical Chemistry. Vol. II. ed. 9. Third printing. pp. 605-609. February, 1942.

MAR 1 1980 OMLY

JUL 26 1960 🔥

