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(57) **Abrégé/Abstract:**

An iron-based oxygen scavenging packet is set forth in which the rate of uptake of oxygen is increased by virtue of the presence of an oxygen uptake accelerator such as water which is introduced into the packet. Methods of increasing the rate of oxygen absorption by the iron-based oxygen scavenging packet are also set forth.



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(21) International Application Number: PCT/US98/02532 (22) International Filing Date: 6 February 1998 (06.02.98) (30) Priority Data: 08/856,448 14 May 1997 (14.05.97) US (71) Applicant: TENNECO PACKAGING INC. [US/US]; 1900 West Field Court, Lake Forest, IL 60045 (US). (72) Inventors: DELDUCA, Gary; 82 Howell Street, Canandaigua, NY 14424 (US). DEYO, Alan, E.; 66 South Main Street, Rushville, NY 14544 (US). LUTHRA, Vindod, K.; 21 Barrington Hills, Pittsford, NY 14534 (US). WU, Wen, P.; 4 Silver Pines Drive, Pittsford, NY 14534 (US). (74) Agent: BOLDINGH, Mary Jo; Arnold, White & Durkee, P.O. Box 4433, Houston, TX 77210 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: OXYGEN SCAVENGER ACCELERATOR (57) Abstract <p>An iron-based oxygen scavenging packet is set forth in which the rate of uptake of oxygen is increased by virtue of the presence of an oxygen uptake accelerator such as water which is introduced into the packet. Methods of increasing the rate of oxygen absorption by the iron-based oxygen scavenging packet are also set forth.</p>		

OXYGEN SCAVENGER ACCELERATOR

5 FIELD OF THE INVENTION

The present invention relates generally to a device and method for maximizing the rate of oxygen uptake of an oxygen absorber. More particularly, the invention relates to an iron based oxygen scavenging packet having an improved composition for accelerating the rate of oxygen absorption wherein the packet is specifically designed to
10 be used in a packaging system designed to keep meat fresh.

BACKGROUND OF THE INVENTION

Perishable foods, such as meats, fruits, and vegetables are typically placed into packaging systems after harvesting in order to preserve these foods for as long as possible. Maximizing the time in which the food remains preserved, especially the time
15 between initial packaging at the plant and delivery at the retail grocery store, increases the profitability of all entities in the chain of distribution by minimizing the amount of spoilage.

The environment in which the food is preserved is a critical factor in the preservation process. Not only is maintaining an adequate temperature important, but the
20 molecular and chemical content of the gases surrounding the food is important as well. By providing an appropriate gas content to the environment surrounding the food, the food can be better preserved when maintained at the proper temperature or even when it is exposed to variations in temperature. This gives the food producer some assurance that after the food leaves his or her control, the food will be in an acceptable condition
25 when it reaches the retail grocery store and ultimately, the consumer.

In meat packaging, in particular, packaging systems which provide extremely low levels of oxygen are desirable because it is well known that the fresh quality of meat can be preserved longer under anaerobic conditions than under aerobic conditions.

Maintaining low levels of oxygen minimizes the growth and multiplication of aerobic bacteria.

One way to insure a minimal level of oxygen in a meat package is to subject the package or rigid gas barrier materials to a vacuum in order to remove as much of the gas in the package as possible prior to sealing the package. The package can then be sealed and the meat maintained in a "zero" atmosphere environment (commonly referred to as vacuum packaging). Under vacuum packaging conditions, red meat turns purple. Consumers, however, prefer to see their meat bright red. As a result, vacuum packaging has not been well accepted for consumer cuts of meat.

Another means of insuring a minimal level of oxygen in a meat package is to seal the meat in a refill modified atmosphere packaging system. This kind of modified atmosphere packaging technology (MAP) is so successful that meat can be cut and packaged several weeks before purchase and still remain fresh. Such systems typically utilize multiple layers of packaging. The outside layer of packaging is generally a rigid container with good barrier properties. The inner layer of packaging is an oxygen permeable film. To provide a modified atmosphere environment, the air-evacuated package is typically filled with a mixture of gases consisting of about 30 percent carbon dioxide (CO₂) and 70 percent nitrogen (N₂). Refilling the air-evacuated package with such a mixture of gases is believed to suppress the growth of anaerobic bacteria. The outer layer is peeled off just prior to presenting the consumer cut for sale at the supermarket. This allows the meat to rebloom to a bright red color. An excellent example of such an evacuation and refill MAP process is described in U.S. Patent No. 5,115,624 to Garwood. Vacuum packaging and refill MAP is very expensive for three reasons. First, the rigid part of the package is expensive. Second, processing speeds are slow due to the vacuum and refill steps. And third, the equipment to do these procedures is very complicated and expensive.

Another less expensive means of insuring a minimal level of oxygen in a meat package is to use a gas flush MAP process. The complicated steps of evacuating the package and refilling with the desired gas mixture are eliminated. The outer bag (a barrier layer), is simply flushed with the proper gas mixture as it is formed around the inner container. The flush process reduces the oxygen content of the package to about two percent. An oxygen scavenger is placed in the package to absorb additional oxygen

just prior to or simultaneously with forming and flushing the outer bag. An excellent example of such a MAP system is described in US Patent 5,698,250 entitled "Modified Atmosphere Package".

A critical feature of a gas flush MAP packaging system is the ability to keep meat
5 looking fresh and palatable. Oxidized meat turns an undesirable brown color. Accordingly, as discussed, an oxygen scavenger is typically placed inside the meat package in order to absorb any residual oxygen within the package after gas flushing and sealing the package. It is critically important to quickly remove the oxygen from meat to prevent it from turning brown. Especially important in preventing the irreversible
10 change from red to brown is the *rate* at which oxygen is scavenged. If oxygen is removed quickly, the packaged meat turns a purple red color. This purple red color quickly "blooms" to a bright red color upon removal of the outer layer of packaging.

Oxygen scavengers are increasingly being used in packaging systems in order to protect various products from the detrimental effects of oxygen exposure. Several
15 oxygen scavengers utilize the oxidation of particulate iron as a method to absorb oxygen. A small amount of water is essential for this reaction. In some instances, a water attracting agent such as silica gel can be used to attract water and at times to supply water in the packet initially. A major drawback to this technology is, however, the limited amount of water that can be supplied. Typically, a major portion of the water needed for
20 the oxidation of particulate iron is provided by the product and/or packaging environment being protected. This is oftentimes an inadequate amount to promote the efficient and expedient oxidation of iron. And as mentioned, the slower the rate of oxygen reduction, the more likely meat will turn irreversibly brown.

A need thus exists to accelerate the rate of oxygen scavengers, particularly in the
25 confines of a modified atmosphere packaging system. Optimally, it would be desirable to lower the oxygen level to about 0.04 percent (400 PPM) within 90 minutes and to about zero within 24 hours. This need will be addressed by the present invention.

SUMMARY OF THE INVENTION

The present invention provides an iron-based oxygen scavenging packet which
30 exhibits an increased rate of oxygen absorption especially in the confines of a concomitant meat packaging system. The invention specifically provides an oxygen

scavenging packet which comprises an iron-based oxygen absorber and an oxygen uptake accelerator comprising water. The oxygen uptake accelerator accelerates the rate of oxygen uptake of the iron-based absorber. In a preferred embodiment, the invention provides an oxygen scavenging packet where a ratio of between .2 ml and .8 ml of
5 oxygen uptake accelerator to about 2.5 grams of iron is present in the packet. Plain water makes an excellent accelerator but preferably, acetic acid is the accelerator of choice. Optimally, approximately .6 ml of oxygen uptake accelerator per 2.5 grams of iron is present in the packet.

More specifically, the present invention provides an oxygen scavenging packet
10 for use in a modified atmosphere package, comprising (a) a plurality of side walls defining an enclosed space, (b) an oxygen absorber within the enclosed space, the oxygen absorber comprising iron, silica gel, and a carbon dioxide generator, and (c) a liquid oxygen uptake accelerator located within a separate compartment within the enclosed space, the oxygen uptake accelerator comprising water, wherein the separate
15 compartment within the enclosed space is capable of being ruptured, wherein the contents of the separate compartment consist essentially of the liquid oxygen uptake accelerator, wherein the liquid oxygen uptake accelerator is present in the packet in an amount in the range of from about 0.2 ml to about 0.8 ml for each approximately 2.5 grams of iron, and wherein a packet containing approximately 5 grams of iron is capable
20 of reducing the oxygen concentration in a quart-sized modified atmosphere package, consisting essentially of air having about 2% oxygen and about 20% carbon dioxide, to less than about 0.5% oxygen in about 90 minutes at about 34° F immediately after the oxygen absorber comes into contact with the oxygen uptake accelerator.

The present invention also provides a method for reducing the oxygen
25 concentration in a modified atmosphere package which comprises an oxygen sensitive material, the method comprising the steps of (a) placing an oxygen scavenging packet in the package, the oxygen scavenging packet comprising (i) a plurality of side walls defining an enclosed space, and (ii) an oxygen absorber within the enclosed space, the oxygen absorber comprising iron, silica gel, and a carbon dioxide generator, (b)

introducing a liquid oxygen uptake accelerator comprising water directly onto the oxygen absorber, and (c) immediately sealing the modified atmosphere package, wherein the amount of liquid oxygen uptake accelerator which is introduced into the packet is an amount in the range of from about 0.2 mL and about 0.8 ml for each 2.5 grams of iron.

5 The present invention also provides a method for minimizing metmyoglobin formation in fresh meat which is contained within a modified atmosphere package, comprising the steps of (a) placing an oxygen scavenging packet in the package, the oxygen scavenging packet comprising (i) a plurality of side walls defining an enclosed space, and (ii) an oxygen absorber within the enclosed space, the oxygen absorber
10 comprising iron, silica gel, and a carbon dioxide generator, (b) introducing a liquid oxygen uptake accelerator comprising water directly onto the oxygen absorber, and (c) immediately sealing the modified atmosphere package, wherein the amount of liquid oxygen uptake accelerator which is introduced into the packet is an amount in the range of from about 0.2 mL and about 0.8 mL for each 2.5 grams of iron.

15 The present invention also provides an oxygen scavenging packet, comprising (a) an oxygen permeable material formed into a closed packet for holding an oxygen absorber, (b) an oxygen absorber comprising iron within the packet of (a), and (c) a liquid oxygen uptake accelerator, the accelerator comprising water, the accelerator being present in an amount relative to the amount of the oxygen absorber, such that when the
20 liquid accelerator and oxygen absorber are brought into contact, the oxygen absorber is capable of reducing the oxygen content of a predetermined volume containing about 2 vol % oxygen to less than 0.5 vol % oxygen at a temperature of about 34° F in no more than 90 minutes after the accelerator and oxygen absorber are brought into contact.

 The present invention also provides a method of reducing the oxygen
25 concentration in an enclosed space comprising (a) placing an oxygen scavenging packet within the enclosed space, the oxygen scavenging packet comprising (i) an oxygen permeable material formed into a closed packet, and (ii) an oxygen absorber within the closed packet, the oxygen absorber comprising iron, and (b) introducing a liquid oxygen uptake accelerator comprising water directly onto the oxygen absorber, wherein the

liquid oxygen uptake accelerator is introduced in an amount relative to the amount of the oxygen absorber, such that when the oxygen uptake accelerator and oxygen absorber are brought into contact, the oxygen absorber is capable of reducing the oxygen content of a predetermined volume containing about 2 vol % oxygen to less than 0.5 vol % oxygen at
5 a temperature of about 34° F in no more than 90 minutes after the oxygen uptake accelerator and oxygen absorber are brought into contact.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and advantages of the invention will become apparent upon reading
10 the following detailed description and upon reference to the drawings in which:

FIG. 1 illustrates an oxygen scavenging packet in which the oxygen uptake accelerator is being introduced into the packet via a syringe.

FIGS. 2a and 2b, respectively, illustrate an oxygen scavenging packet containing a capsule which can be ruptured at an appropriate time to release the oxygen uptake
15 accelerator and a packet containing a capsule being ruptured.

FIGS. 3a and 3b, respectively, illustrate an oxygen scavenging packet including a protruding wick for absorption of the oxygen uptake accelerator into the packet and an oxygen scavenging packet in which the wick is being dipped into the oxygen scavenger
accelerator.

20 FIG. 4 is an isometric view of the oxygen scavenging packet of the instant invention inside a modified atmosphere packaging system.

FIG. 5 is a graph illustrating the rate of oxygen absorption when a dry oxygen scavenging packet is introduced into a quart sized container which also includes 0.5 ml of water.

25 FIG. 6 is a graph illustrating the rate of oxygen absorption when an oxygen scavenging packet having 0.5 ml of water injected into the packet is introduced into a quart sized container.

FIG. 7 is a graph illustrating the rate of oxygen absorption as a function of the amount of water injected into oxygen scavenging packets.

FIG. 8 illustrates the rate of oxygen absorption in the presence of varying amounts of CO₂ utilizing an oxygen scavenging packet which has been injected with 0.6 ml of water.

FIG. 9 is a graph illustrating the rate of oxygen absorption as a function of the number of oxygen scavenging packets introduced into a one quart jar.

FIG. 10 is a graph showing the percent oxygen after 1 hour as a function of the amount of acetic acid (vinegar) injected into each of two oxygen scavenging packets.

FIG. 11 is a graph showing the percent oxygen as a function of time and as a function of the material injected into the oxygen scavenging packets.

FIG. 12 is a graph illustrating the rate of oxygen absorption as a function of the amount of acetic acid injected into an iron containing packet and further as a function of whether or not the packet contains impregnated silica gel.

FIG. 13 is a graph illustrating the rate of oxygen absorption as a function of time and the concentration of acetic acid in water.

While the invention is susceptible to various modifications and alternative forms, certain specific embodiments thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular forms described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Turning now to the drawings, FIGS. 1 through 3 (a and b) depict an oxygen scavenging packet having a liquid oxygen uptake accelerator present in some form within the packet.

Specifically, FIG. 1 depicts an oxygen scavenging packet 10 containing elemental iron 12 and in which an oxygen uptake accelerator 14 is introduced into the packet utilizing a syringe 16. Injection can be performed manually with a syringe and hand placement of the packet inside the package. Alternatively, the injection process can be automated by using a commercially available metering and dispensing pump such as the Luft Systematic model 45/50 and appropriate conveying equipment to position the packets for injection and then subsequently to place the packets into a package.

FIG. 2a depicts an oxygen scavenging packet 20 containing elemental iron 22 and in which an oxygen uptake accelerator 24 is present inside a capsule 26. As FIG. 2b shows, the capsule 26 may be ruptured by mechanical force at an appropriate time in order to release the oxygen uptake accelerator 24. Optimally, the capsule should be
5 ruptured immediately prior to or immediately after the sealing of the package in order to properly activate the iron-based scavenger for accelerated oxygen uptake.

FIG. 3a depicts an iron-based oxygen scavenging packet 30 containing elemental iron (not specifically shown) and in which an oxygen uptake accelerator 32 can be introduced into the packet by absorption onto a wick 34 which protrudes from the packet.
10 As FIG. 3b shows, the wick 34 dipped into the oxygen uptake accelerator 32. An appropriate amount of oxygen uptake accelerator 32 is absorbed through the wick 34 into the packet 30. Optimally, the dipping occurs immediately prior to the sealing of the package in order to properly activate the iron based scavenger for accelerated oxygen uptake.

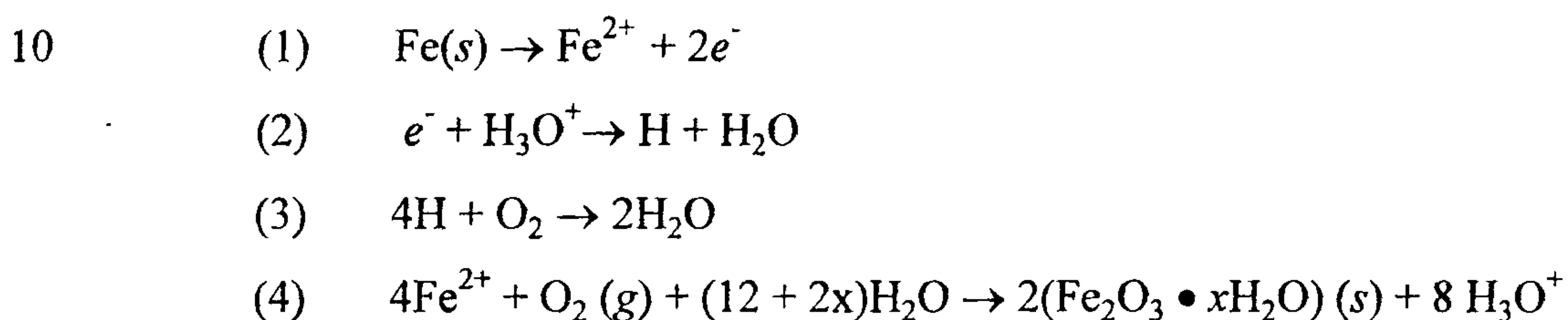
15 Further information concerning the construction of the oxygen absorber packet preferred for use in the instant invention may be obtained from U.S. Patent No. 5,262,375 to McKedy, entitled "Oxygen Absorber." The preferred oxygen absorber packets are manufactured by Multiform Desiccants Incorporated. However, other iron-based oxygen absorbers will work comparably well in the instant invention.

20 The instant invention particularly concerns an iron-based oxygen scavenging packet which contains an oxygen uptake accelerator consisting of water or an aqueous solution of some other substance dissolved in or mixed with water. The oxygen uptake accelerator accelerates the rate of oxygen uptake of the oxygen absorber. Water alone will activate and accelerate iron-based oxygen absorbers via the presence of hydronium
25 ions in the water. However, dilute acid solutions are preferred oxygen uptake accelerators.

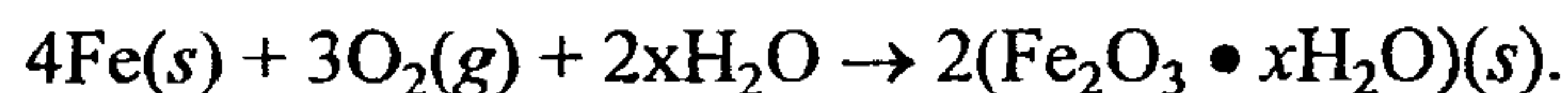
Acids provide increased numbers of hydronium ions which increase the oxidation rate of iron by acting as electron acceptors. These electron acceptors facilitate the ionization of neutral iron. Once ionized, the iron readily reacts with the available oxygen
30 and water to form a hydrated iron oxide. Other electron acceptors such as the positively charged ions making up salt solutions or metals such as copper also facilitate the ionization of neutral iron.

The preferred aqueous solution of the instant invention is an aqueous solution which contains approximately five percent acetic acid.

The introduction of water or an aqueous solution of acid, salt or appropriate metal into the oxygen absorber packet of an iron-based oxygen absorber serves to activate and dramatically increase the rate of oxygen uptake of the iron inside the packet. The particulate iron in the packet, in effect, turns to rust as oxygen is absorbed from the atmosphere surrounding the packaged meat or other packaged food product. As discussed, the water or aqueous solution enhances oxygen absorption by the iron by acting as an electron acceptor. A proposed mechanism for rust formation is as follows:



In step (1) ferrous ions are produced by loss of electrons from the elemental particulate iron in the packet. However, this process cannot go very far unless there is some way to get rid of the electrons which accumulate on the residual Fe. One way to do this is by step (2) in which H_3O^{+} ions either from the water or from acid substances in the water, pick up the electrons to form neutral H atoms. Since Fe is known to be a good catalyst for hydrogenation reactions in general, it is believed that step (3) now occurs to use up the H atoms. In the meantime, the ferrous ion reacts with O_2 gas by step (4) to form the rust and restore H_3O^{+} required for step (2). The net reaction, obtained by adding all four steps is



Acid accelerates the reaction by providing excess hydronium ions (H_3O^{+}) and driving step 2. Therefore, the preferred embodiment of the present invention utilizes a dilute aqueous solution of acid. Such acid solutions should, of course, be compatible with food products and include, for instance, acetic acid and/or citric acid.

Salt solutions also drive step (2) of the aforementioned reaction by providing an electron acceptor, thus they are suitable for use in the aqueous solution of the instant invention. Additionally, it has been found that adding copper to water and/or dilute

aqueous solution of acid speeds the rate of oxygen absorption by the iron. It is believed that the copper induces a phenomena called electrolytic corrosion. Electrons flow from the iron to the copper, where their energy is lower. This removes the excess negative charge from the iron. In addition H atoms, which now form on the negative copper
5 surface instead of the iron, detach themselves more readily from copper than from iron, thus accelerating step (3) of the aforementioned reaction.

As shown in FIGS. 1-3 (a and b), the aqueous solution can be introduced into the packet utilizing an injection type process. Alternatively, the solution can be included in the absorber packet in a separate capsule or compartment which can be ruptured at the
10 time of sealing the meat package. Also, a wick could be included in, and protrude from, the packet such that the wick could be dipped in liquid just prior to sealing the meat package.

A preferred embodiment of the present invention involves the injection of an oxygen uptake accelerator comprising water into the MRM absorbers manufactured by
15 Multiform Desiccants Incorporated. This is done just prior to the placement of the absorber into a package. This can be done manually with a syringe and hand placement or the process can be automated by using a commercially available metering and dispensing pump such as the Luft Systematic model 45/50 and appropriate conveying equipment to position the packets for injection and then subsequently to place the packets
20 into a package.

The following data, depicted in FIGS. 5-13 and in Table 1 is specific to Multiform's MRM 100 scavenger packets. All of these experiments involve using these scavengers. The MRM 100 oxygen scavengers are specifically formulated to work in the presence of CO₂ and refrigeration. MRM 100 oxygen scavengers contain approximately
25 2.5 grams of iron and silica gel impregnated with a carbon dioxide generator, NaHCO₃. A carbon dioxide generator is utilized to replace gas volume in the sealed meat package as O₂ is absorbed. The iron in MRM absorbers is electrolytically reduced and annealed which means that the iron is reduced by the passage of electric current through a solution of the iron which is in the form of a molten salt. As one skilled in the art will appreciate,
30 while MRM 100 scavenger packets were used in the following described experiments, similarly constituted scavenger packets would be expected to have comparably enhanced oxygen scavenging activities with the addition of water and other accelerators.

FIGS. 5 and 6 illustrate that the oxygen uptake accelerator, in this case water, must be contained within the oxygen scavenging packet in order to increase the rate of oxygen absorption. Specifically, FIG. 5 shows the decrease in percent oxygen as a function of time when 0.5 ml of water is merely present in a quart-sized jar along with an oxygen scavenging packet. As shown in FIG. 5, at 40°F it takes approximately 30 hours for the percent oxygen to be reduced to approximately 0.5% (5,000 PPM) and more than 40 hours for the percent oxygen to be reduced to near 0.0% oxygen. By contrast, FIG. 6 shows the decrease in percent oxygen as a function of time when 0.5 ml of water is injected into an oxygen scavenging packet which is then placed in a quart-sized jar. At 40°F, it takes approximately 15 hours for the percent oxygen to be reduced to approximately 0.5% and about 20 hours for the percent oxygen to be reduced to near 0.0% oxygen. At 70°F, oxygen is scavenged much more quickly.

FIG. 7 shows that the oxygen scavenging rate is maximized when 0.6 ml of water is present in the oxygen scavenging packet.

FIG. 8 shows that oxygen absorption appears to be independent of the amount of carbon dioxide in the container.

FIG. 9 shows that two oxygen scavenging packets absorb oxygen at nearly twice the rate of one packet.

As shown in FIG. 10, acetic acid, commonly known as vinegar acid, works particularly well in accelerating the rate of oxygen absorption of an MRM oxygen scavenger packet. Specifically, the injection of .5 ml. of acetic acid into each of two absorber packets reduces the amount of oxygen in a quart jar to approximately .1% O₂ (1000 PPM) in one hour. As shown in FIG. 11, the percent O₂ is reduced to approximately .04% O₂ (400 PPM) in about ninety minutes when .5 ml. of acetic acid is injected into each of two MRM 100 scavenger packets. Two conclusions can be drawn from the data in FIGS. 10 and 11. First, injected acetic acid seems to work better than plain water in increasing the rate of oxygen absorption of an absorber packet. Second, from FIG. 10, .5 ml. acetic acid appears to work particularly well in increasing the rate and total amount of oxygen absorption. In the experiments resulting in the data in FIGS. 10 and 11, the starting level of oxygen in the jars was 2.0%, simulating the amount of oxygen which would be present after the gas flush step of a gas flush MAP process. Also, the experiments were performed under refrigeration.

Below is a table which shows the results of an experiment designed to determine the range of amounts of water needed to be introduced into an oxygen scavenging packet containing approximately 2.5 grams of iron in order to satisfactorily activate the packets in a gas flush MAP packaging process for red meat.

5 **TABLE 1**

Sample No.	Water Injection	Initial Oxygen	Final Oxygen	Color Rating - 1.5 hrs. Of Bloom (Day 8)	Color Rating - 24 hrs. Of Bloom (Day 9)
1	.8 ml	1.9%	0.00%	Dark Red	Some Browning
2	.6 ml	1.24%	0.00%	Dark Red	Bright Red
3	1.0 ml	2.30%	0.26%	Major Browning	Major Browning
4	.4 ml	2.20%	0.00%	Dark Red	Bright Red
5	.2 ml	1.70%	0.00%	Dark Red	Dark Red
6	.4 ml	1.50%	14.9%	Excluded (Leaked)	Excluded
7	.8 ml	1.70%	0.00%	Dark Red	Dark Red
8	.6 ml	1.55%	0.00%	Dark Red	Bright Red
9	1.0 ml	2.20%	0.00%	Dark Red	Some Browning
10	.2 ml	2.40%	0.00%	Major Browning	Major Browning

The results show that water injections greater than .2 ml but less than .8 ml per 2.5 grams of iron (approximately 100cc of absorber capacity) are required. For adequate oxygen scavenging, water injections must be within this range, preferably at .6 milliliters. Water injections outside of this range will result in a high risk of metmyoglobin formation (browning) due to initial oxygen exposure. This experiment was performed utilizing Multifirm's MRM oxygen scavengers but other similar iron-based absorbers are believed to work comparably.

EXAMPLE 1 - Determination of Range of Water Volume Necessary for Optimal Oxygen Scavenging of an Iron Based Oxygen Scavenging Packet

15 A ten pound chunk of fresh boneless beef (five days post mortem) was cut into ten pieces and individually placed on meat trays or a soaker pad. The meat trays had one and one half inch tall side walls. The meat and trays were then stretch wrapped with a standard PVC film on a Hobart machine. After wrapping, a half inch diameter hole was created through

the PVC in one corner of the tray to allow free flow of gases in and out of this "inner package." Next, two MRM 100 scavengers were injected with a precisely measured amount of water and attached to one of the inner packages containing the beef. The water injections were varied from .2 to 1.0 mils per scavenger. The inner package, with the oxygen absorbers attached, was then immediately run through a Fuji/Foremost form fill and seal machine and packaged in a flushed outer bag made from Print Pack 861D 2.5 mil barrier film. The flush gas was approximately 80% nitrogen and 20% carbon dioxide. The initial O₂ level in the barrier bag was measured through a rubber septum with a Dansensor oxygen analyzer and recorded. The completed packages were then placed in a refrigerator and stored at 34°F for eight days. On the eight day the final oxygen level was measured and the barrier bag and oxygen absorbers removed. The meat was allowed to rebloom in the inner package for one and a half hours in the refrigerator. At that time the packages were removed from the refrigerator and the meat visually rated for color acceptability. The packages were then returned to the refrigerator for another 24 hours after which the meat was again rated for color acceptability.

The tray that was used for the experiment detailed in Example 1 and the data detailed in Table 1 left a significant amount of air space surrounding the meat, necessitating the use of two MRM 100 scavengers. However, beef has been successfully packaged on shallow wall meat trays using only one MRM 100 scavenger with a .5 ml injection of acetic acid.

FIG. 12 shows that maximum oxygen absorption occurs at an amount of vinegar between about .4 and .6 ml acetic acid. FIG. 12 also illustrates that maximum oxygen absorption occurs when the oxygen scavenging packet contains silica gel impregnated with NaHCO₃ in addition to iron. MRM-100 absorbers and other similarly formulated absorbers employ silica gel to absorb and release atmospheric H₂O. As discussed previously, silica gel will not by itself absorb enough water to satisfactorily accelerate the oxygen scavenging ability of the iron to allow for the preservation of meats for longer

than a few days at a time. For this reason, the present inventors have affirmatively added concrete amounts of water to the oxygen scavenging packets of the instant invention.

FIG. 13 shows the rate of oxygen absorption as a function of time and the concentration of acetic acid in water. As can be seen, 5% acetic acid performs very well at accelerating the rate of oxygen absorption at 30, 60 and 90 minutes. Furthermore, 5% acetic acid is very easy to obtain, being common table vinegar.

The present invention is particularly useful when used in a modified atmosphere packaging (MAP) process for fresh meats. The MAP process is a gas flush process that initially flushes the package to an oxygen atmosphere of about two percent or less. The oxygen scavenging packet of the instant invention is utilized to additionally reduce the oxygen level of the package to 400 PPM (0.04%) or less within ninety minutes.

A brief description of the typical modified atmosphere package will follow. This description is not meant to be limiting, but instead is provided merely to elucidate one particular use for the instant invention.

FIG. 4 depicts a modified atmosphere package 40 including an outer container 42 and an inner container 44. The inner container 44 includes a conventional semi-rigid plastic tray 46 thermoformed from a sheet of polymeric material which is substantially permeable to oxygen. Exemplary polymers which may be used to form the non-barrier tray 46 include polystyrene foam, cellulose pulp, polyethylene, polypropylene, etc. In a preferred embodiment, the polymeric sheet used to form the tray 46 is substantially composed of polystyrene foam and has a thickness ranging from about 100 mils to about 300 mils. The use of a common polystyrene foam tray 46 is desirable because it has a high consumer acceptance. The inner container 44 further includes a stretch film wrapping or cover 48 substantially composed of a polymeric material, such as polyvinyl chloride (PVC), which is substantially permeable to oxygen. In a preferred embodiment, the stretch film used to form the cover 48 contains additives which allow the film to cling to itself and has a thickness ranging from about 0.5 mil to about 1.5 mils. One preferred stretch film is Resinite™ meat film commercially available from Borden Packaging and Industrial Products of North Andover, Massachusetts.

A food item such as a retail cut of raw meat 50 is located inside the inner container 44. Prior to fully wrapping the tray 46 with the cover 48, the partially formed inner container 44 may be flushed with an appropriate mixture of gases, typically a

mixture of about 30 percent carbon dioxide and about 70 percent nitrogen, to lower the oxygen level in the inner container 44 to about 1.5 to 5.0 percent. The foregoing mixture of gases displaces the oxygen within the inner container 44 during the flushing operation. After flushing the inner container 44, the tray 46 is manually or automatically wrapped
5 with the cover 48. The cover 48 is wrapped over the retail cut of raw meat 50 and about the bottom of the tray 46. The free ends of the cover 48 are overlapped along the underside of the bottom wall of the tray 46, and, due to the cling characteristic inherent in the cover 48, these overlapping free ends cling to one another to hold the cover 48 in place. If desired, the overwrapped tray 46, i.e., the inner container 44, may be run over a
10 hot plate to thermally fuse the free ends of the cover 48 to one another and thereby prevent these free ends from potentially unraveling.

The outer container 42 is preferably a flexible polymeric bag composed of a single or multilayer plastics material which is substantially impermeable to oxygen. The outer container 42 may, for example, include an oriented polypropylene (OPP) core
15 coated with an oxygen barrier coating such as polyvinylidene chloride and further laminated with a layer of sealant material such as polyethylene to facilitate heat sealing. In a preferred embodiment, the outer container 42 is composed of a multilayer barrier film commercially available as product no. 325C44-0EX861D from PrintPack, Inc. of Atlanta, Georgia. The co-extruded film has a thickness ranging from about 2 mils to
20 about 6 mils. Prior to sealing the peripheral edges of the outer container 42, the inner container 44 is placed within the outer container 42. Also, the outer container 42 is flushed with an appropriate mixture of gases, typically about 30 percent carbon dioxide and about 70 percent nitrogen, to lower the oxygen level in the outer container 42 to about 0.05 to 5.0 percent or 500 to 50,000 parts per million (PPM). Prior to or
25 simultaneously with flushing the outer container 42, but still prior to sealing the outer container 42, the oxygen scavenging packet 52 is placed in the outer container 42 external to the sealed inner container 44. The outer container 42 is then sealed.

After a time period of about ninety minutes, the oxygen scavenging packet 52 lowers the oxygen level in the bag from its initial level of oxygen to less than about 0.04
30 percent or 400 PPM and most preferably to about zero percent. The oxygen uptake accelerator contained within the oxygen scavenging packet 52 is responsible for this fast rate of oxygen absorption. The oxygen scavenger 52 also absorbs any oxygen which

might permeate into the outer container 42 from the ambient environment. In FIGS. 1 through 4, the oxygen scavenger 10, 20, 30, and 52 respectively, is illustrated as a packet or label which is inserted into the outer container 42 prior to sealing the outer container 42. Alternatively, an oxygen scavenging material may be added to the polymer or
5 polymers used to form the outer container 42 so that the oxygen scavenging material is integrated into the outer container 42 itself.

The retail cut of raw meat 50 within the package 40 takes on a purple-red color when the oxygen is removed from the interior of the package 40. The meat-filled modified atmosphere package 40 may now be stored in a refrigeration unit for several
10 weeks prior to being offered for sale at a grocery store. A short time (e.g., less than one hour) prior to being displayed at the grocery store, the inner container 44 is removed from the outer container 42 to allow oxygen from the ambient environment to permeate the non-barrier tray 46 and non-barrier cover 48. The purple-red color of the raw meat 50 quickly changes or "blooms" to a generally acceptable bright red color when the raw
15 meat 50 is oxygenated by exposure to air.

While the present invention has been described with reference to one or more particular embodiments, those skilled in the art will recognize that many changes may be made thereto without departing from the spirit and scope of the present invention. Each of these embodiments and obvious variations thereof is contemplated as falling within
20 the spirit and scope of the claimed invention, which is set forth in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An oxygen scavenging packet for use in a modified atmosphere package, comprising:
 - (a) a plurality of side walls defining an enclosed space;
 - (b) an oxygen absorber within the enclosed space, said oxygen absorber comprising iron, silica gel, and a carbon dioxide generator; and
 - (c) a liquid oxygen uptake accelerator located within a separate compartment within the enclosed space, said oxygen uptake accelerator comprising water;wherein said separate compartment within the enclosed space is capable of being ruptured;
wherein the contents of said separate compartment consist essentially of the liquid oxygen uptake accelerator;
wherein said liquid oxygen uptake accelerator is present in said packet in an amount in the range of from 0.2 ml to 0.8 ml for each 2.5 grams of iron; and
wherein a packet containing 5 grams of iron is capable of reducing the oxygen concentration in a quart-sized modified atmosphere package, consisting essentially of air having 2% oxygen and 20% carbon dioxide, to less than 0.5% oxygen in 90 minutes at 34° F immediately after the oxygen absorber comes into contact with the oxygen uptake accelerator.
2. The oxygen scavenging packet of claim 1, wherein said oxygen uptake accelerator is present in said packet in an amount between 0.3 ml and 0.7 ml per 2.5 grams of said iron.
3. The oxygen scavenging packet of claim 1, wherein 0.4 to 0.6 ml of said oxygen uptake accelerator is present in said packet per 2.5 grams of said iron.
4. The oxygen scavenging packet of claim 1, wherein 0.6 ml of said oxygen uptake accelerator is present in said packet per 2.5 grams of said iron.

5. The oxygen scavenging packet of any one of claims 1 to 4, wherein said iron is electrolytically annealed and reduced.
6. The oxygen scavenging packet of any one of claims 1 to 5, wherein said oxygen uptake accelerator is contained within a frangible capsule and the oxygen uptake accelerator is introduced directly onto the oxygen absorber by rupturing the frangible capsule.
7. The oxygen scavenging packet of any one of claims 1 to 5; wherein said oxygen uptake accelerator is contained within a bibulous wick, wherein said wick extends from the exterior of said packet, through at least one of said plurality of walls and into said enclosed space.
8. The oxygen scavenging packet of any one of claims 1 to 7, wherein said oxygen uptake accelerator further comprises an acid.
9. The oxygen scavenging packet of claim 8, wherein said acid is citric acid.
10. The oxygen scavenging packet of claim 8, wherein said acid is acetic acid.
11. The oxygen scavenging packet of claim 10, wherein said oxygen uptake accelerator comprises five percent acetic acid.
12. The oxygen scavenging packet of any one of claims 1 to 11, wherein said silica gel is impregnated with the carbon dioxide generator.
13. The oxygen scavenging packet of any one of claims 1 to 12, wherein said packet further comprises a means for introducing said liquid oxygen uptake accelerator directly onto the oxygen absorber.
14. The oxygen scavenging packet of any one of claims 1 to 13, wherein said oxygen uptake accelerator further comprises a salt.

15. The oxygen scavenging packet of claim 14, wherein said salt is selected from the group consisting of NaCl, CaCl₂, and MgCl₂.
16. The oxygen scavenging packet of any one of claims 1 to 15, wherein said oxygen uptake accelerator further comprises copper.
17. A method for reducing the oxygen concentration in a modified atmosphere package which comprises an oxygen sensitive material, the method comprising the steps of:
- (a) placing an oxygen scavenging packet in the package, said oxygen scavenging packet comprising:
 - (i) a plurality of side walls defining an enclosed space; and
 - (ii) an oxygen absorber within the enclosed space, said oxygen absorber comprising iron, silica gel, and a carbon dioxide generator;
 - (b) introducing a liquid oxygen uptake accelerator comprising water directly onto said oxygen absorber; and
 - (c) immediately sealing the modified atmosphere package;
- wherein the amount of liquid oxygen uptake accelerator which is introduced into said packet is an amount in the range of from 0.2 ml and 0.8 ml for each 2.5 grams of iron.
18. The method of claim 17, wherein said oxygen uptake accelerator is present in said packet in an amount between 0.3 ml and 0.7 ml per 2.5 grams of said iron.
19. The method of claim 17, wherein 0.4 to 0.6 ml of said oxygen uptake accelerator is present in said packet per 2.5 grams of said iron.
20. The method of claim 19, wherein 0.6 ml of said oxygen uptake accelerator is present in said packet per 2.5 grams of said iron.
21. The method of any one of claims 17 to 20, wherein the iron is electrolytically annealed and reduced.

22. The method of any one of claims 17 to 21, wherein said oxygen uptake accelerator is contained within a frangible capsule and the oxygen uptake accelerator is introduced directly onto the oxygen absorber by rupturing the frangible capsule.
23. The method of any one of claims 17 to 21, wherein said oxygen uptake accelerator is contained within a bibulous wick, wherein said wick extends from the exterior of said packet, through at least one of said plurality of walls and into said enclosed space.
24. The method of any one of claims 17 to 21, wherein said step of introducing said oxygen uptake accelerator directly onto said oxygen absorber includes injecting said oxygen uptake accelerator onto said oxygen absorber.
25. The method of claim 24, wherein said step of introducing said oxygen uptake accelerator directly onto said oxygen absorber is carried out using a syringe.
26. The method of claim 24, wherein said step of introducing said oxygen uptake accelerator directly onto said oxygen absorber includes placing into said packet a frangible capsule containing the oxygen uptake accelerator, wherein the oxygen uptake accelerator is introduced directly onto the oxygen absorber by rupturing the frangible capsule.
27. The method of any one of claims 17 to 26, wherein said oxygen uptake accelerator further comprises an acid.
28. The method of claim 27, wherein said acid is citric acid.
29. The method of claim 27, wherein said acid is acetic acid.
30. The method of claim 29, wherein said oxygen uptake accelerator comprises five percent acetic acid.

31. The method of any one of claims 17 to 30, wherein said silica gel is impregnated with the carbon dioxide generator.

32. The method of any one of claims 17 to 31, wherein said packet further comprises a means for introducing said liquid oxygen uptake accelerator directly onto the oxygen absorber.

33. The method of any one of claims 17 to 32, wherein said oxygen uptake accelerator further comprises a salt.

34. The method of claim 33, wherein said salt is selected from the group consisting of NaCl, CaCl₂, and MgCl₂.

35. The method of any one of claims 17 to 34, wherein said oxygen uptake accelerator further comprises copper.

36. A method for minimizing metmyoglobin formation in fresh meat which is contained within a modified atmosphere package, comprising the steps of:

(a) placing an oxygen scavenging packet in the package, said oxygen scavenging packet comprising:

(i) a plurality of side walls defining an enclosed space; and

(ii) an oxygen absorber within the enclosed space, said oxygen absorber comprising iron, silica gel, and a carbon dioxide generator;

(b) introducing a liquid oxygen uptake accelerator comprising water directly onto said oxygen absorber; and

(c) immediately sealing the modified atmosphere package;

wherein the amount of liquid oxygen uptake accelerator which is introduced into said packet is an amount in the range of from 0.2 ml and 0.8 ml for each 2.5 grams of iron.

37. The method of claim 36, wherein said oxygen uptake accelerator is present in said packet in an amount between 0.3 ml and 0.7 ml per 2.5 grams of said iron.

38. The method of claim 36, wherein 0.4 to 0.6 ml of said oxygen uptake accelerator is present in said packet per 2.5 grams of said iron.

39. The method of claim 38, wherein 0.6 ml of said oxygen uptake accelerator is present in said packet per 2.5 grams of said iron.

40. The method of any one of claims 35 to 39, wherein the iron is electrolytically annealed and reduced.

41. The method of any one of claims 35 to 40, wherein said oxygen uptake accelerator is contained within a frangible capsule and the oxygen uptake accelerator is introduced directly onto the oxygen absorber by rupturing the frangible capsule.

42. The method of any one of claims 35 to 40, wherein said oxygen uptake accelerator is contained within a bibulous wick, wherein said wick extends from the exterior of said packet, through at least one of said plurality of walls and into said enclosed space.

43. The method of any one of claims 35 to 39, wherein said step of introducing said oxygen uptake accelerator directly onto said oxygen absorber includes injecting said oxygen uptake accelerator onto said oxygen absorber.

44. The method of claim 43, wherein said step of introducing said oxygen uptake accelerator directly onto said oxygen absorber is carried out using a syringe.

45. The method of claim 43, wherein said step of introducing said oxygen uptake accelerator directly onto said oxygen absorber includes placing into said packet a frangible capsule containing the oxygen uptake accelerator, wherein the oxygen uptake accelerator is introduced directly onto the oxygen absorber by rupturing the frangible capsule.

46. The method of any one of claims 35 to 45, wherein said oxygen uptake accelerator further comprises an acid.

47. The method of claim 46, wherein said acid is citric acid.
48. The method of claim 46, wherein said acid is acetic acid.
49. The method of claim 48, wherein said oxygen uptake accelerator comprises five percent acetic acid.
50. The method of any one of claims 35 to 49, wherein said silica gel is impregnated with the carbon dioxide generator.
51. The method of any one of claims 35 to 50, wherein said packet further comprises a means for introducing said liquid oxygen uptake accelerator directly onto the oxygen absorber.
52. The method of any one of claims 35 to 51, wherein said oxygen uptake accelerator further comprises a salt.
53. The method of claim 52, wherein said salt is selected from the group consisting of NaCl, CaCl₂, and MgCl₂.
54. The method of any one of claims 35 to 53, wherein said oxygen uptake accelerator further comprises copper.
55. An oxygen scavenging packet, comprising:
- (a) an oxygen permeable material formed into a closed packet for holding an oxygen absorber;
 - (b) an oxygen absorber comprising iron within the packet of (a); and
 - (c) a liquid oxygen uptake accelerator, said accelerator comprising water, said accelerator being present in an amount relative to the amount of said oxygen absorber, such that when the liquid accelerator and oxygen absorber are brought into contact, the oxygen absorber is capable of reducing the oxygen content of a predetermined volume

containing 2 vol % oxygen to less than 0.5 vol % oxygen at a temperature of 34° F in no more than 90 minutes after said accelerator and oxygen absorber are brought into contact.

56. An oxygen scavenging packet of claim 55, wherein said oxygen absorber of (b) further comprises silica gel and a carbon dioxide generator.

57. An oxygen scavenging packet of claim 55 or 56, wherein said iron is electrolytically annealed and reduced.

58. An oxygen scavenging packet of claim 55, 56 or 57, wherein said oxygen uptake accelerator further comprises a salt.

59. An oxygen scavenging packet of any one of claims 55 to 58, wherein said oxygen uptake accelerator further comprises an acid.

60. An oxygen scavenging packet of any one of claims 55 to 59, wherein said oxygen uptake accelerator is contained within an enclosed space within said packet.

61. An oxygen scavenging packet of any one of claims 55 to 60, wherein said oxygen uptake accelerator is contained within a bibulous wick, said wick extending from the exterior of said packet into the interior of said packet.

62. A method of reducing the oxygen concentration in an enclosed space comprising:

(a) placing an oxygen scavenging packet within said enclosed space, said oxygen scavenging packet comprising:

(i) an oxygen permeable material formed into a closed packet; and

(ii) an oxygen absorber within said closed packet, said oxygen absorber comprising iron; and

(b) introducing a liquid oxygen uptake accelerator comprising water directly onto said oxygen absorber, wherein said liquid oxygen uptake accelerator is introduced in an amount relative to the amount of said oxygen absorber, such that when the oxygen uptake accelerator and oxygen absorber are brought into contact, the oxygen absorber is capable of reducing the oxygen content of a predetermined volume containing 2 vol % oxygen to

less than 0.5 vol % oxygen at a temperature of 34° F in no more than 90 minutes after said oxygen uptake accelerator and oxygen absorber are brought into contact.

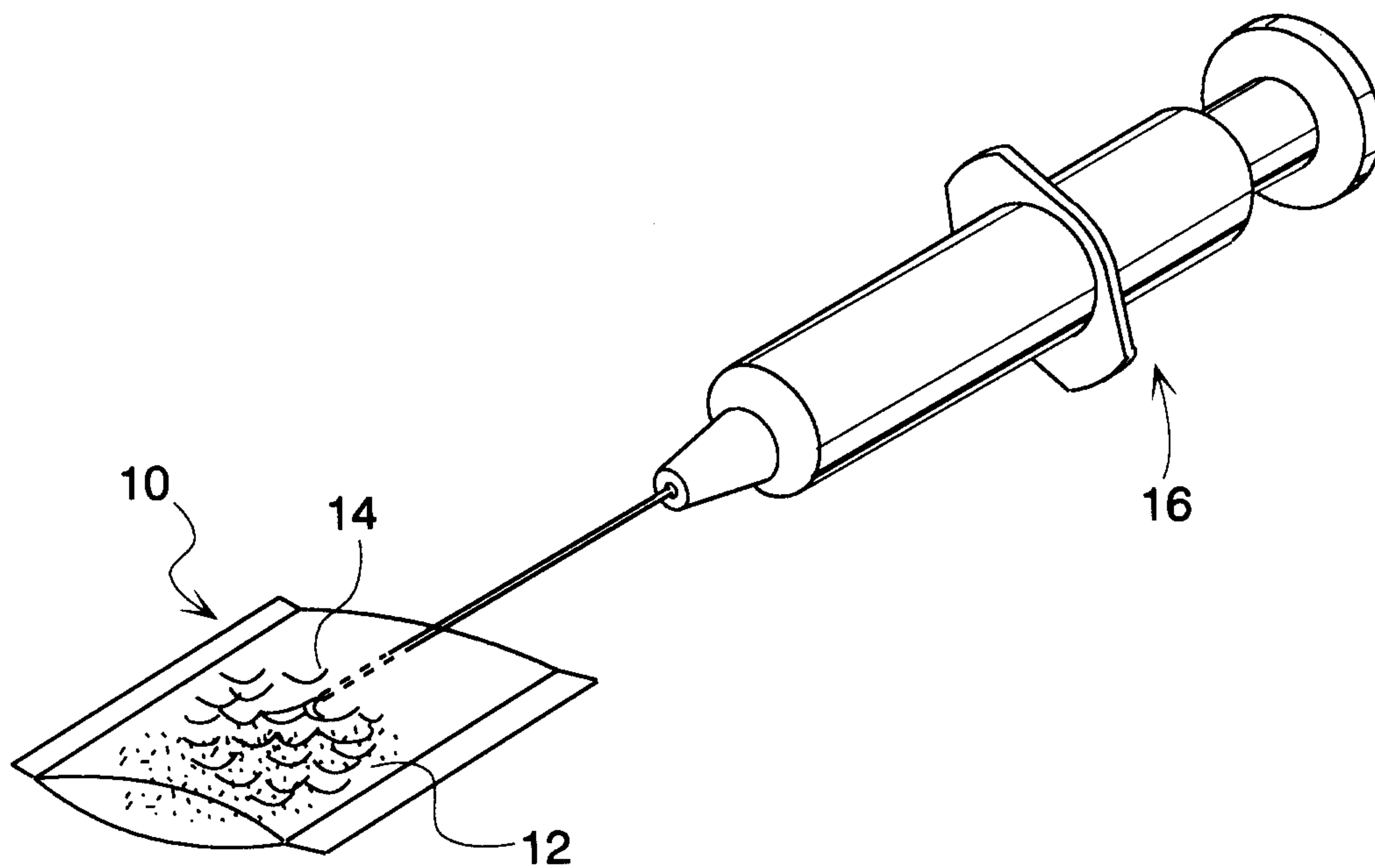
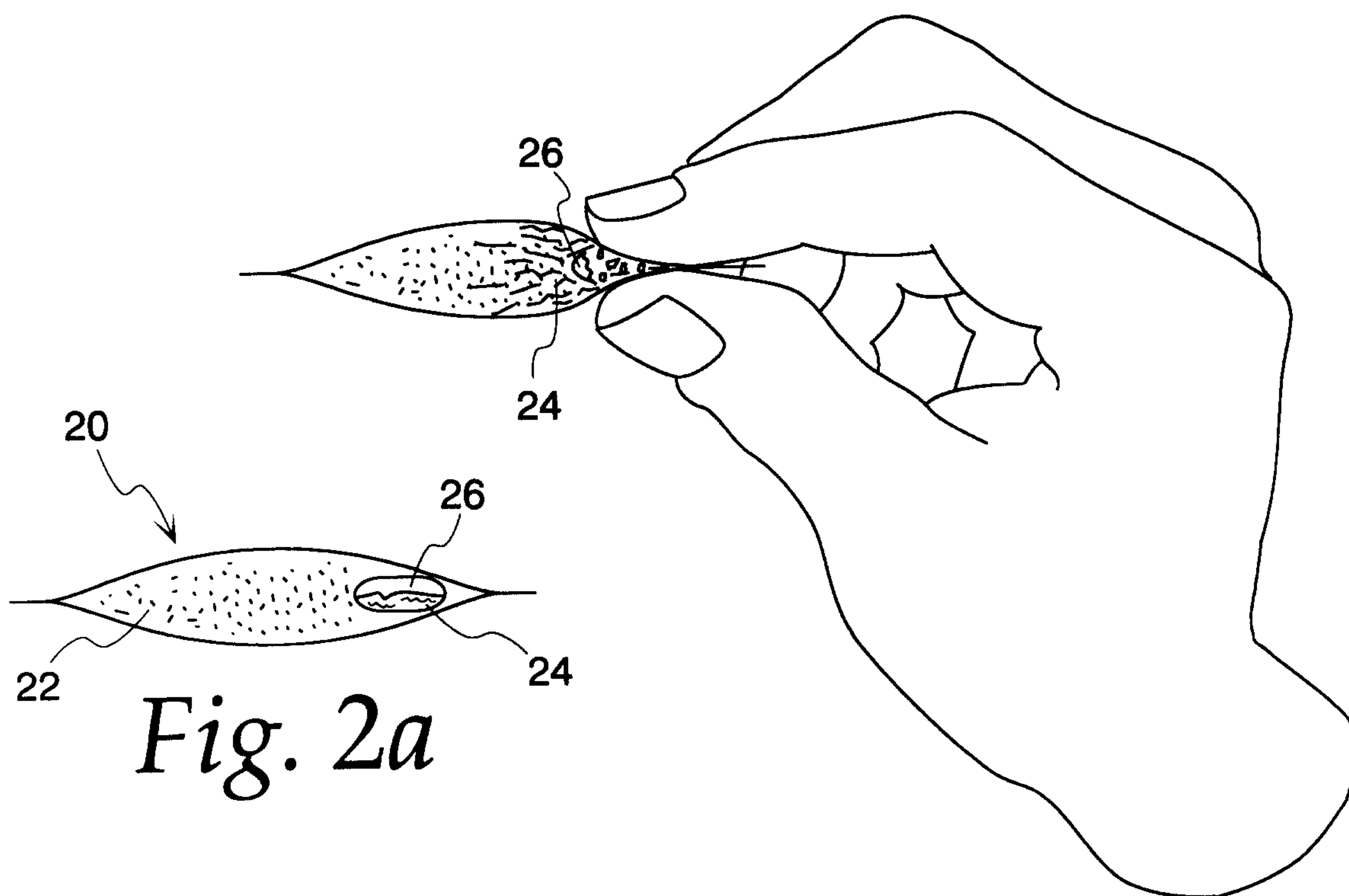
63. A method of claim 62, wherein said oxygen absorber further comprises silica gel and a carbon dioxide generator.

64. A method of claim 62 or 63, wherein said oxygen uptake accelerator further comprises a salt.

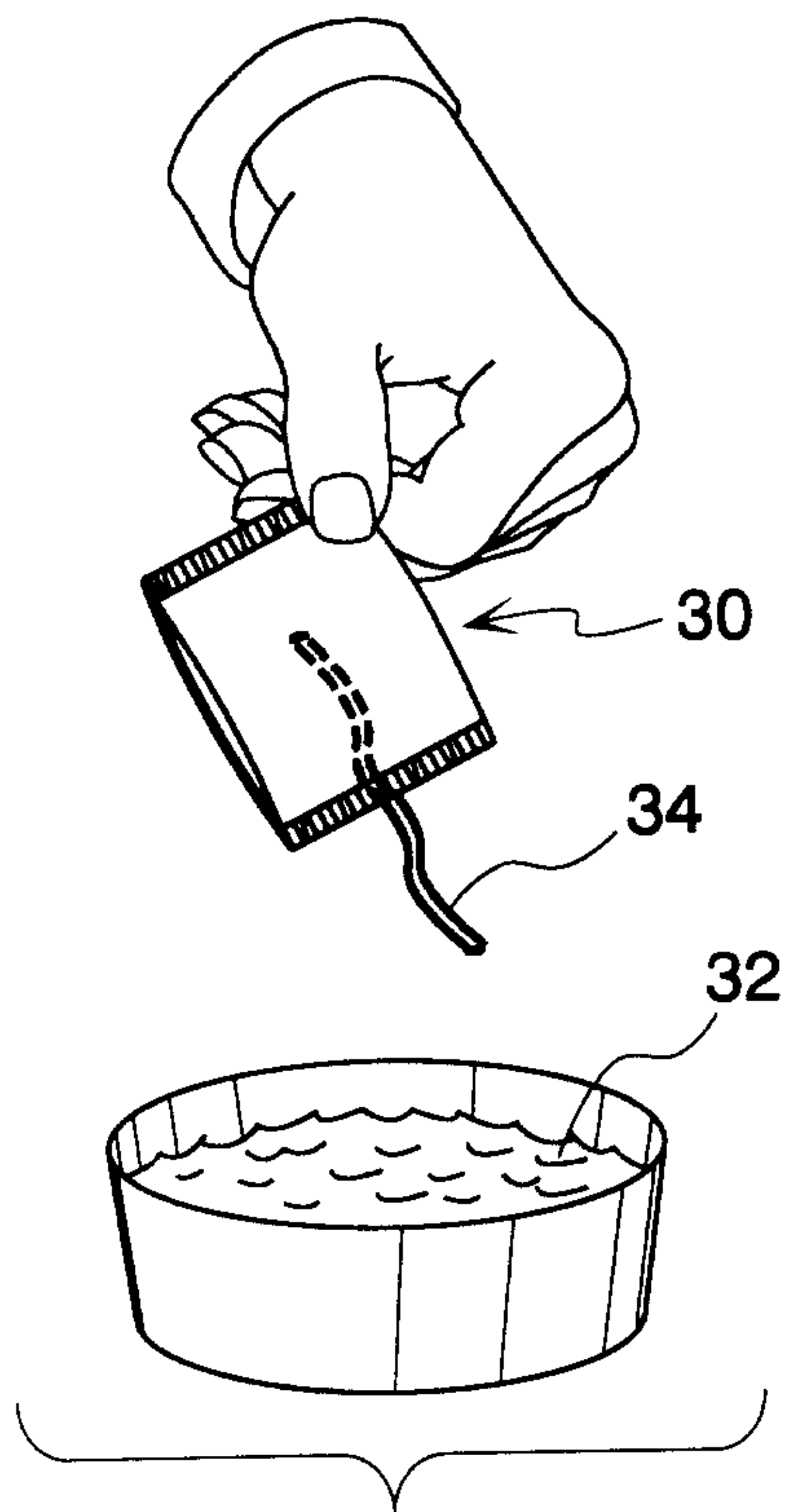
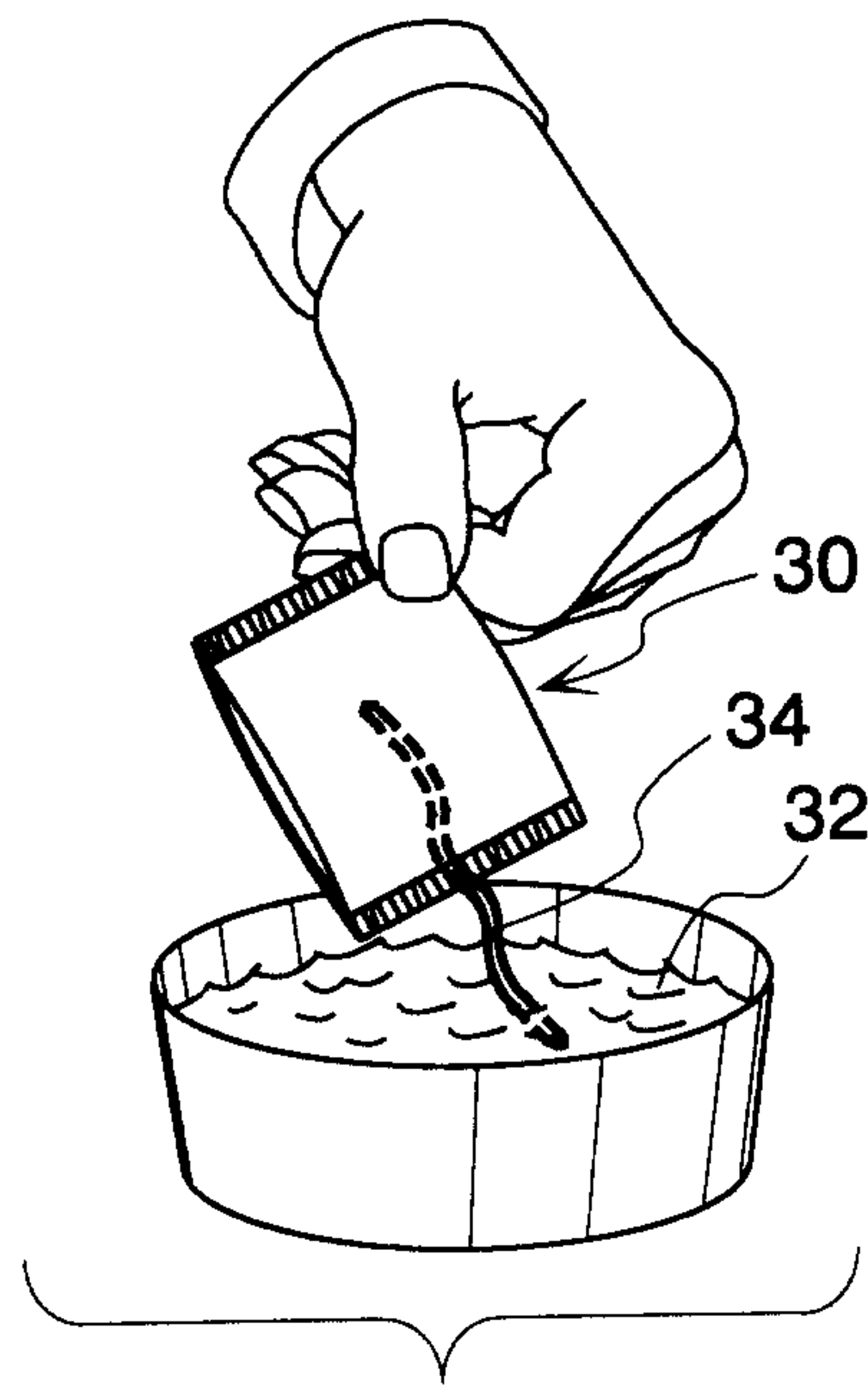
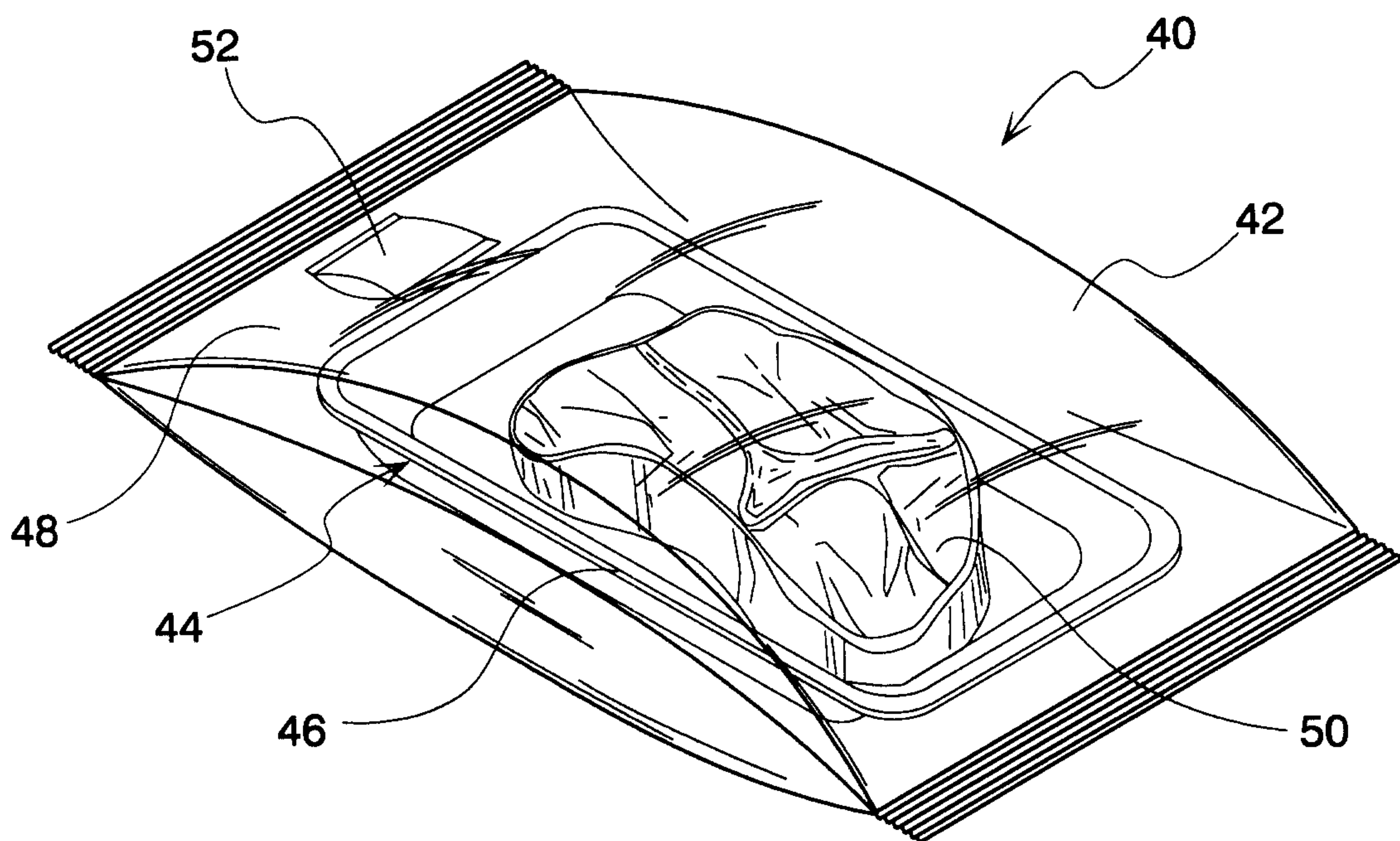
65. A method of claim 62, 63 or 64, wherein said iron is electrolytically annealed and reduced.

66. A method of any one of claims 62 to 65, wherein said oxygen uptake accelerator further comprises an acid.

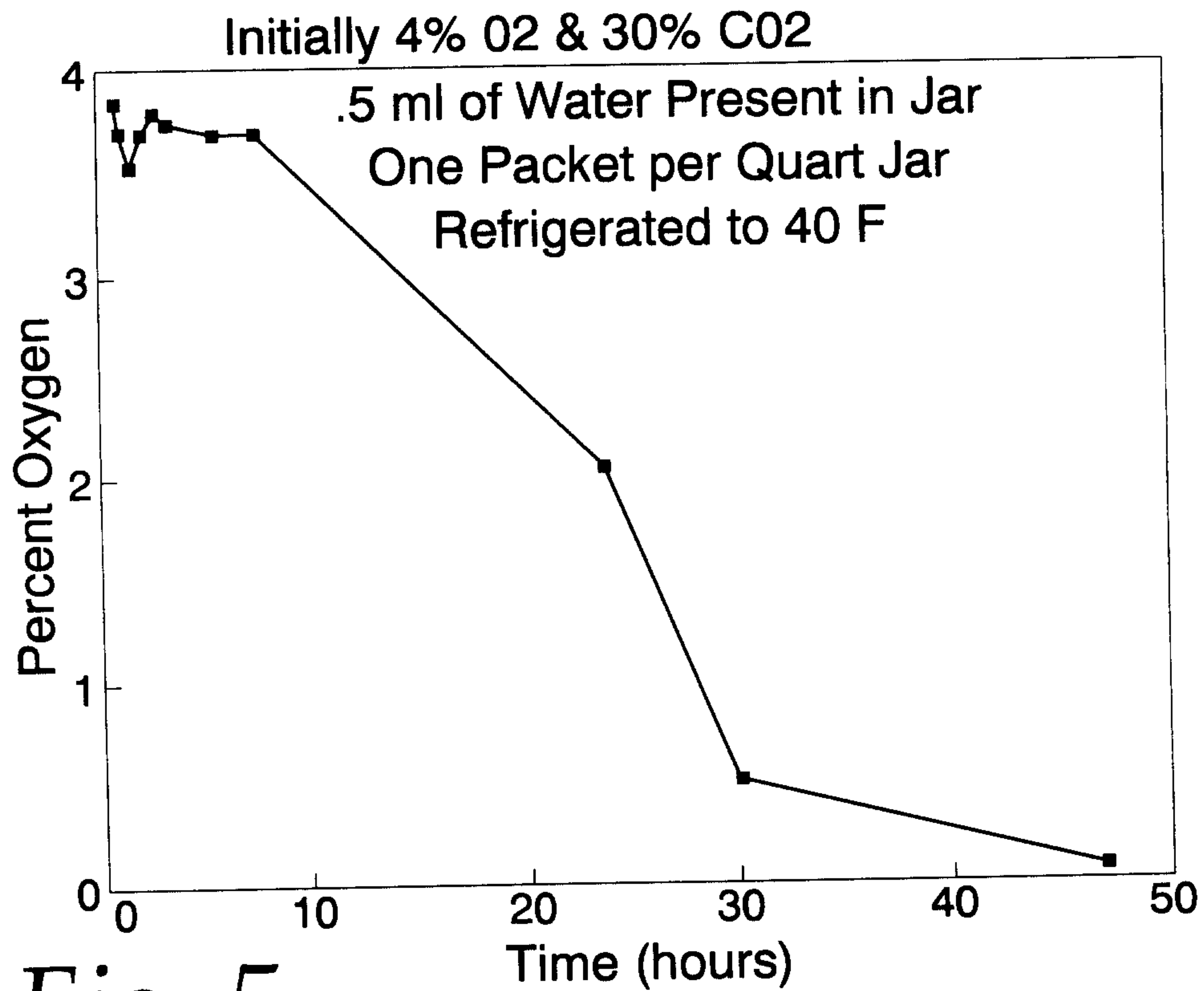
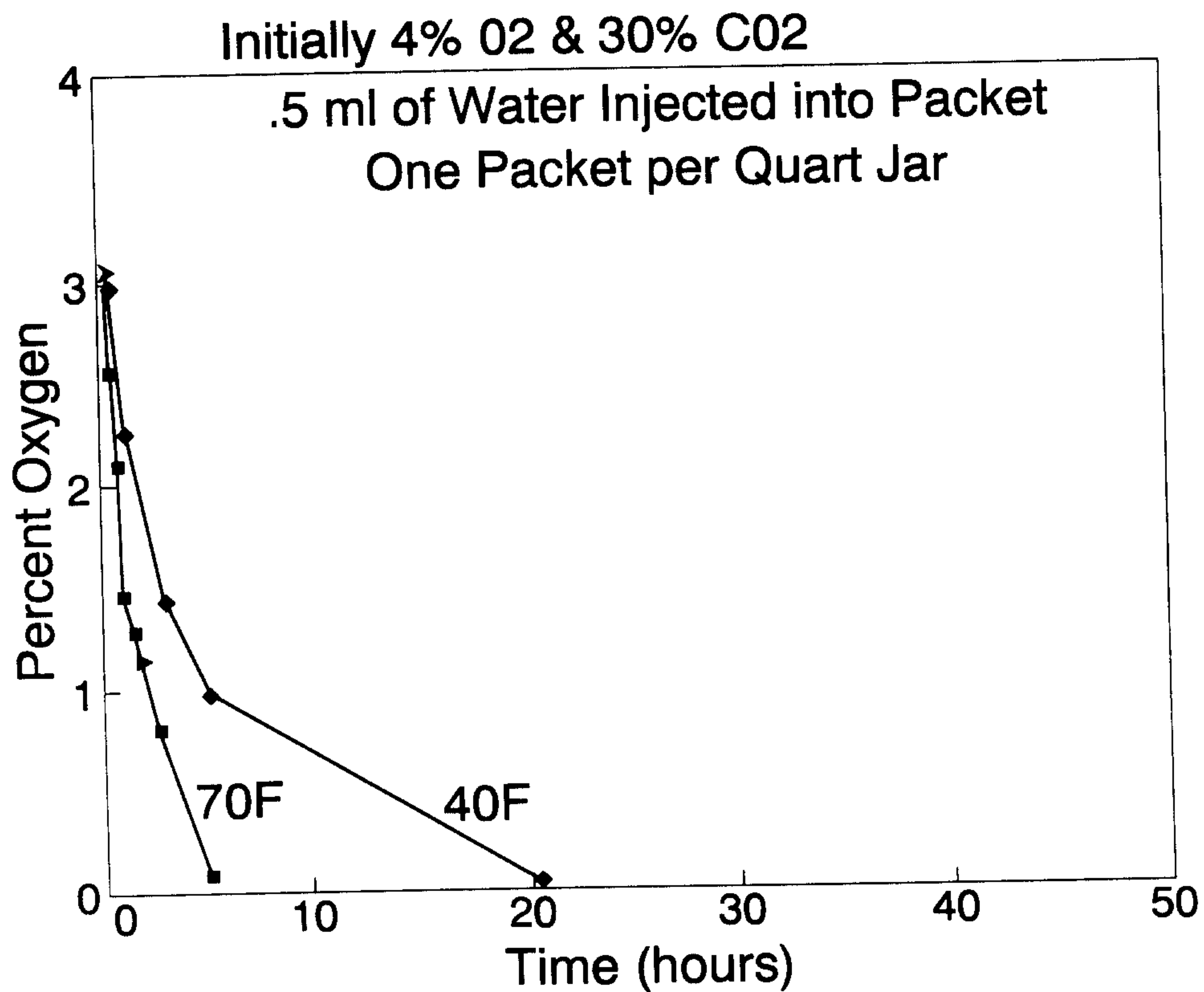
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*Fig. 1**Fig. 2b**Fig. 2a**Maria V. Clerk*

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*Fig. 3a**Fig. 3b**Fig. 4**Marko & Clerk*

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*Fig. 5**Fig. 6**Mark & Clerk*

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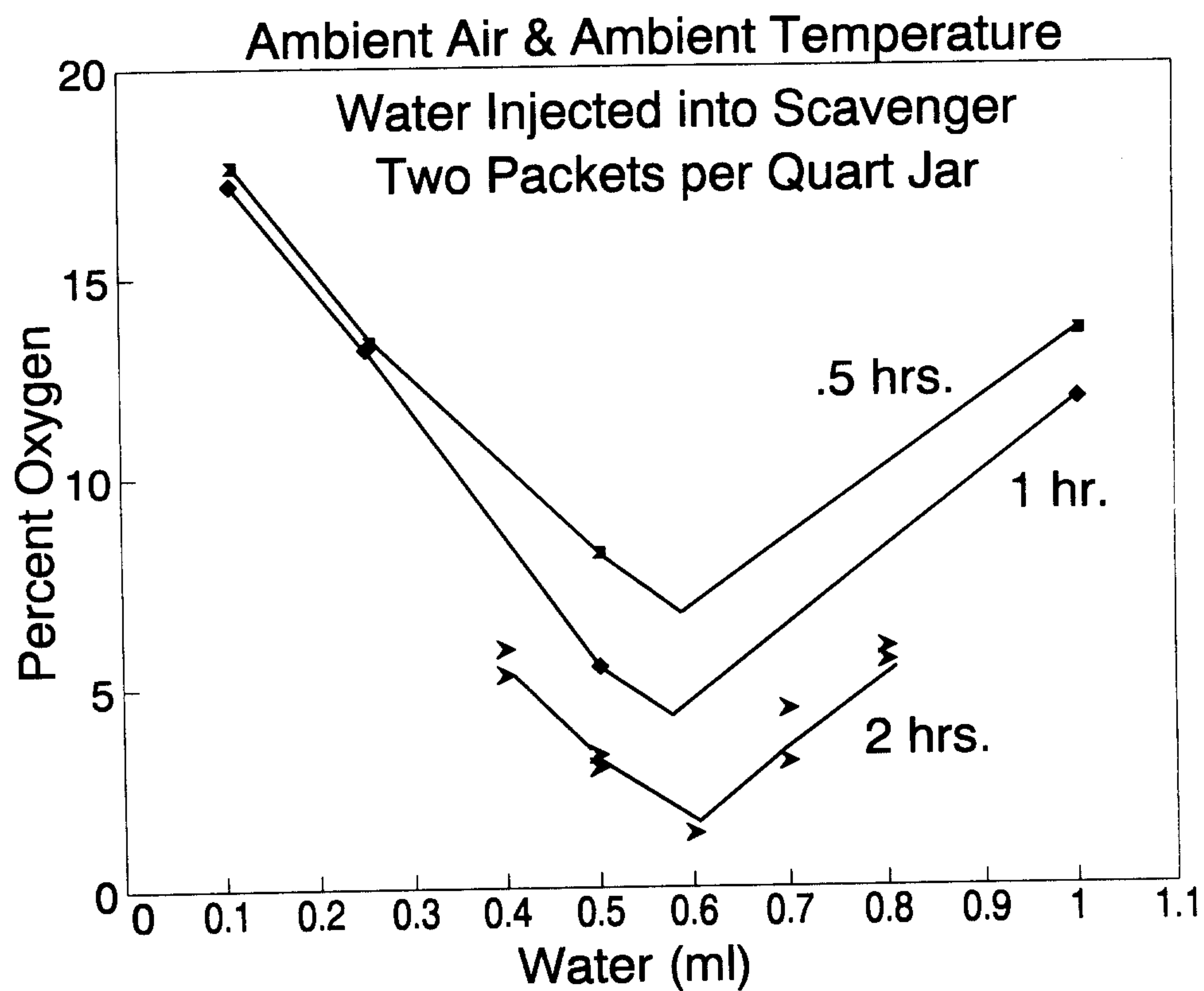


Fig. 7

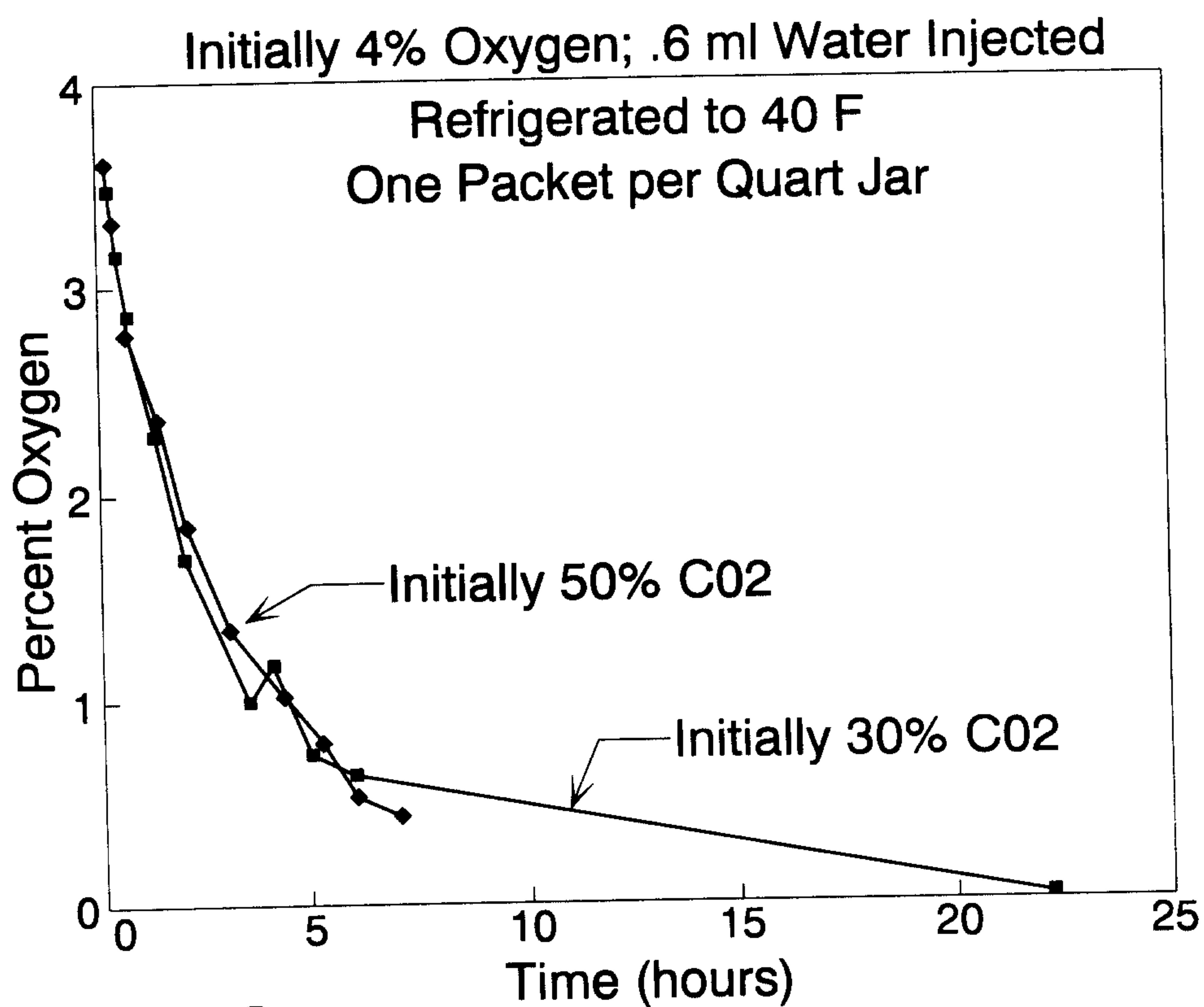
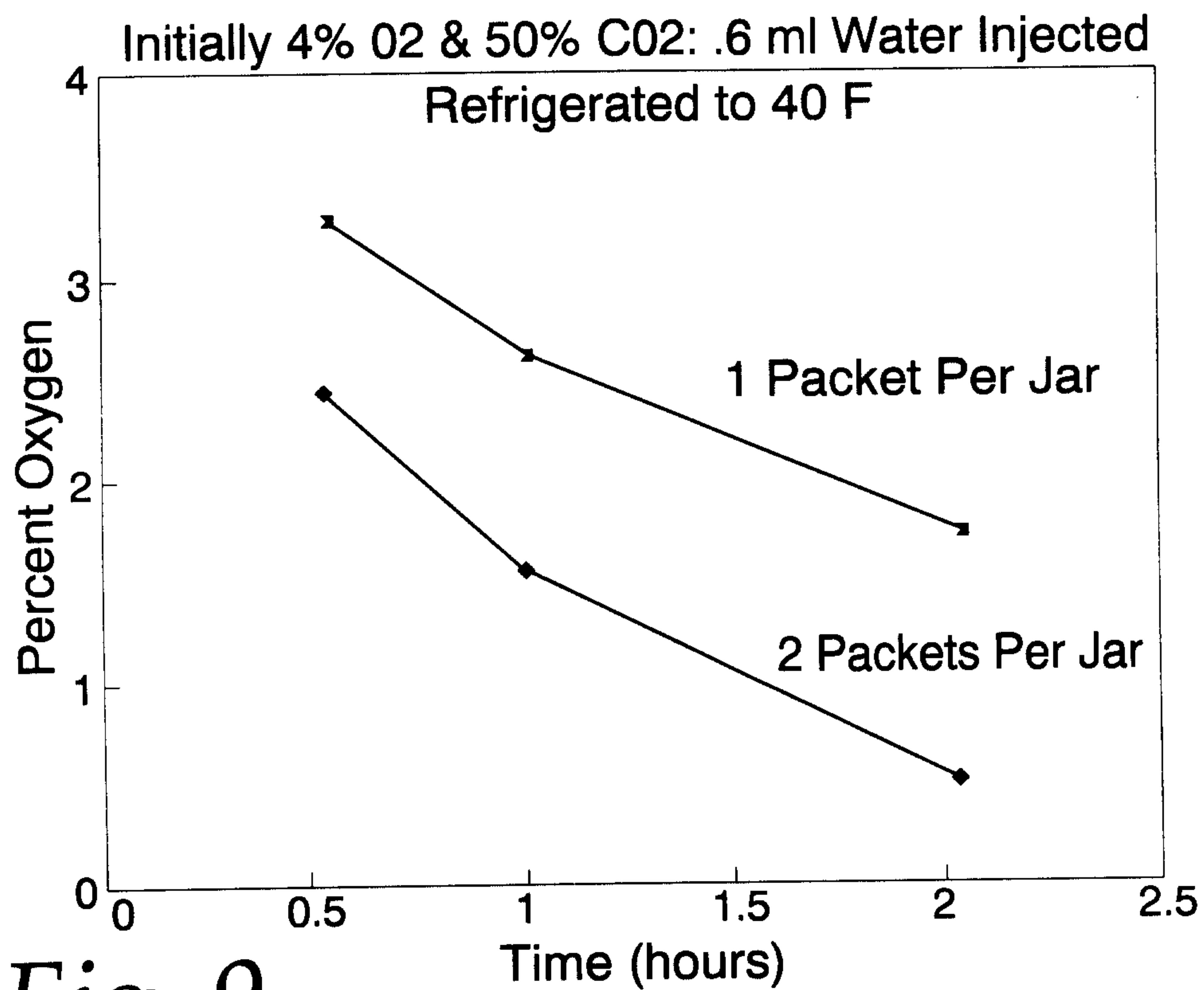
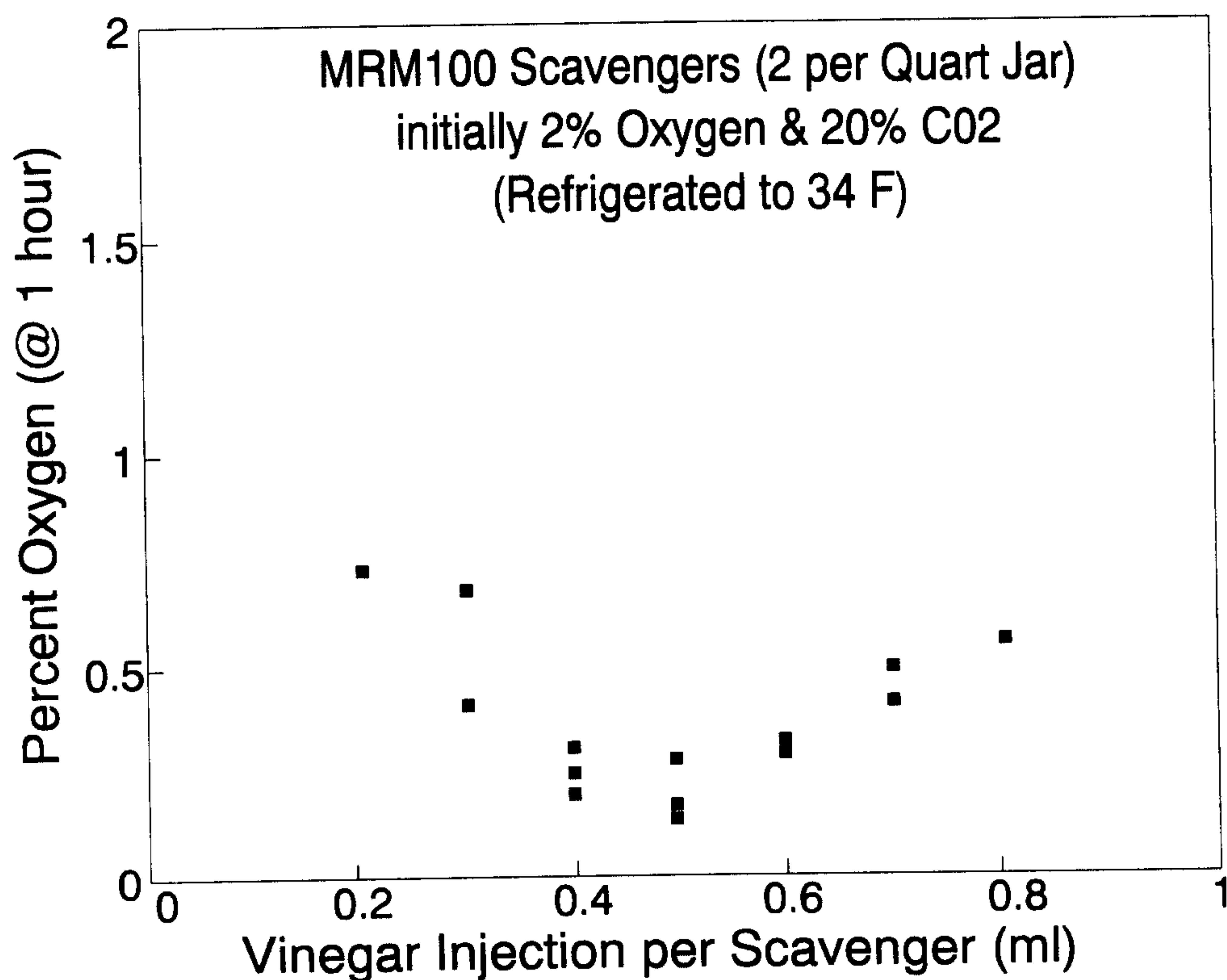


Fig. 8

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*Fig. 9**Fig. 10**Mark & Clark*

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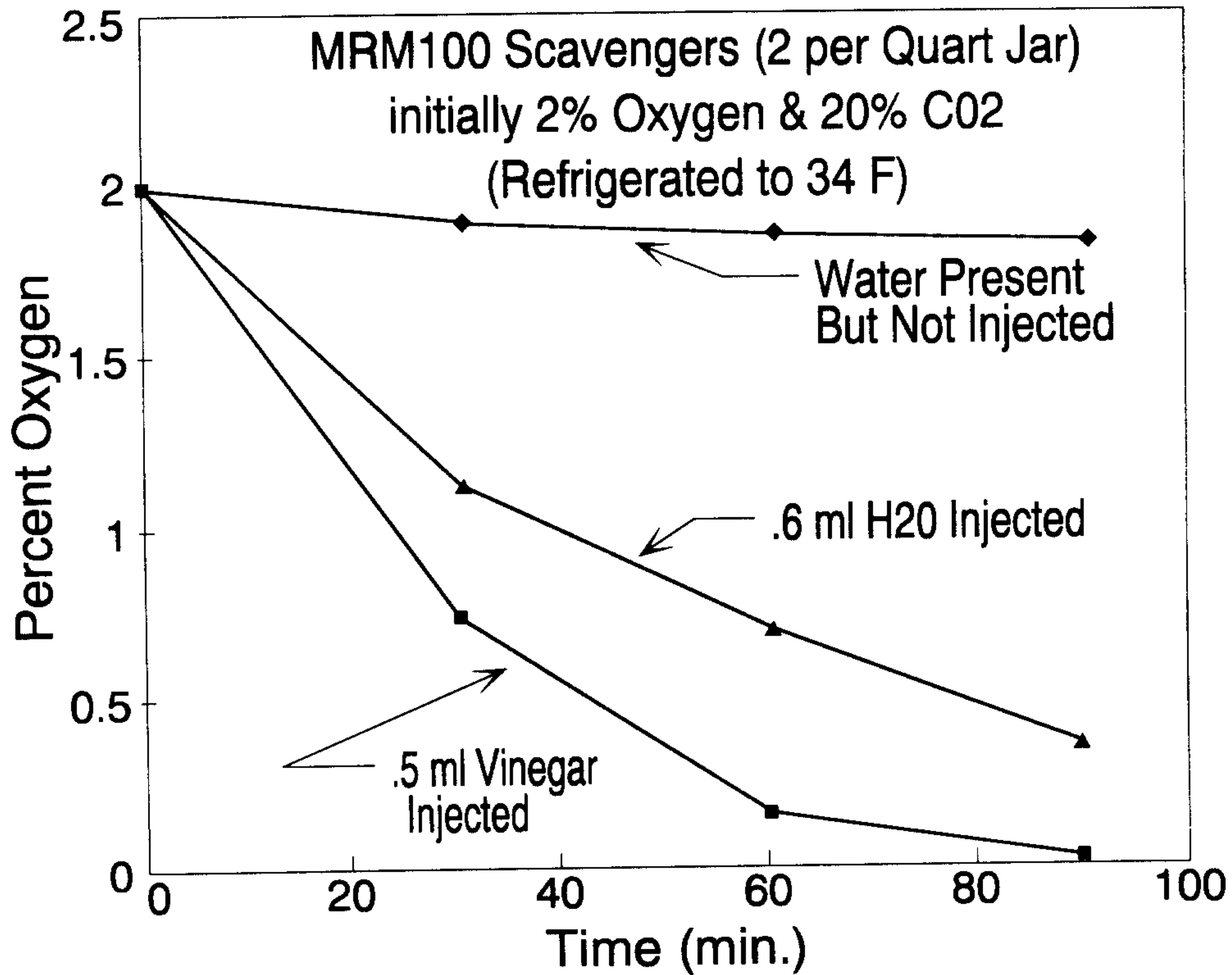


Fig. 11

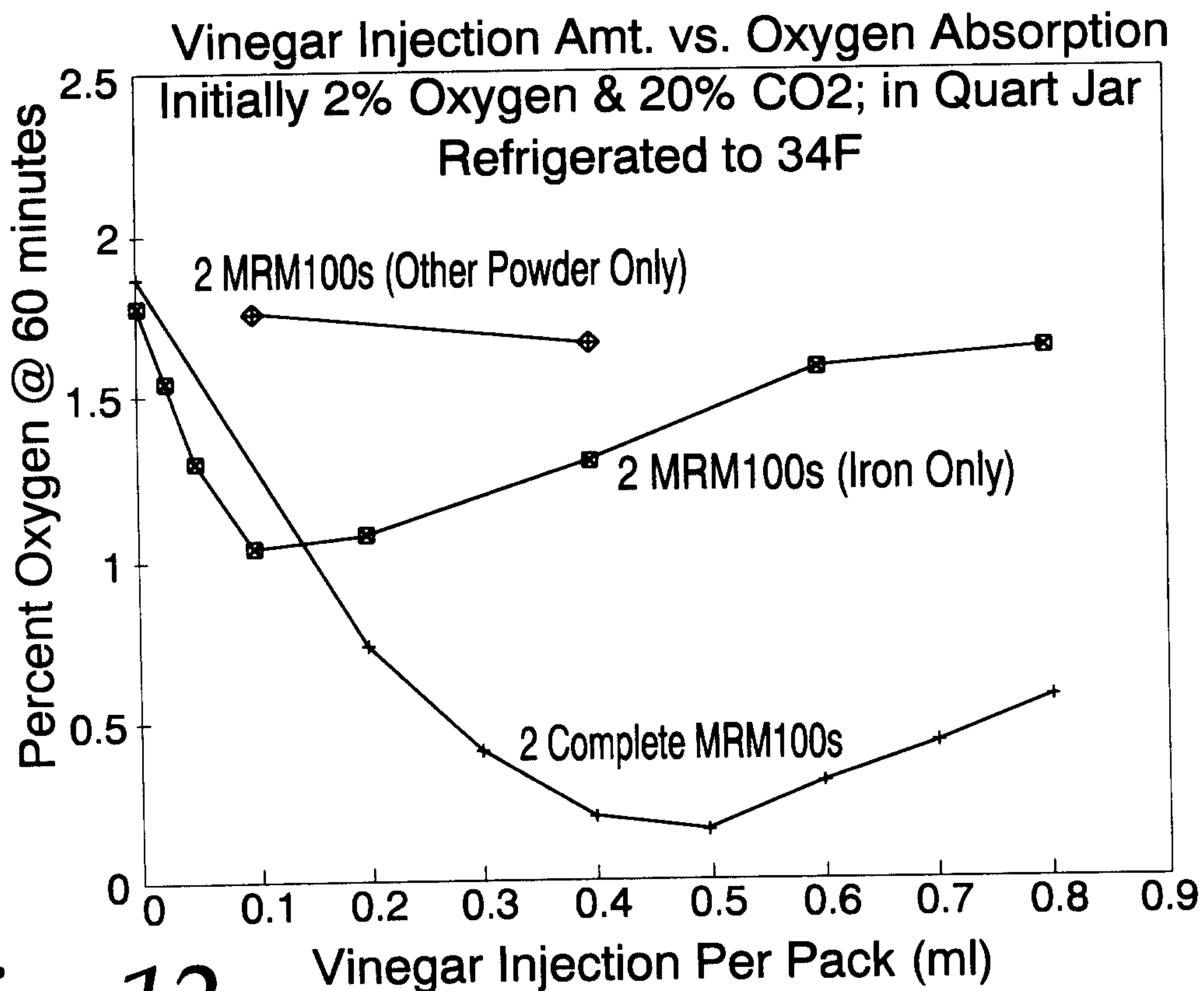
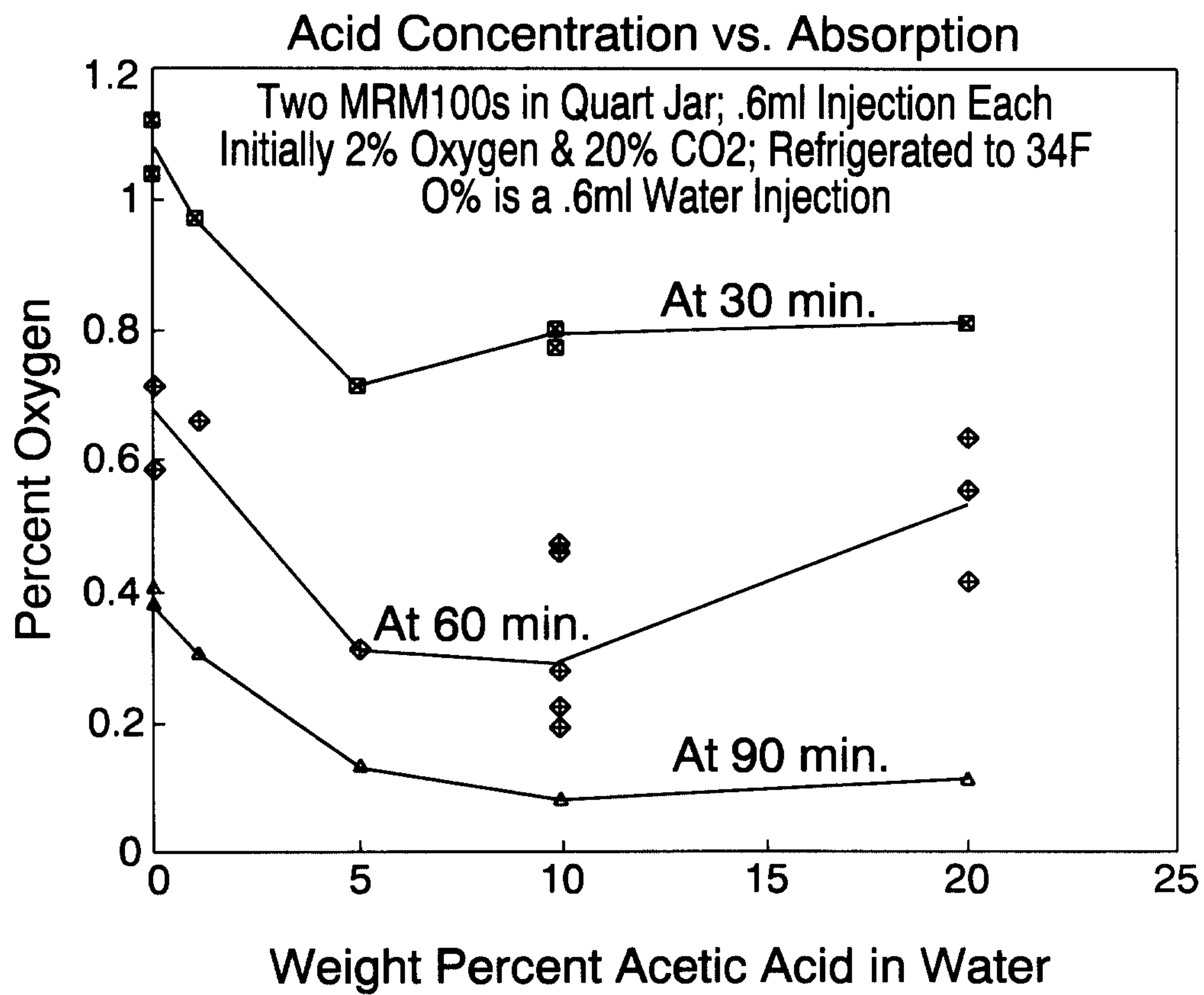


Fig. 12

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*Fig. 13**Marks & Clerk*