

DESCRIPTION

OFF FLAVOR CONTROLLING METHOD IN RAW MILK AND PASTEURIZED MILK, AND PASTEURIZED MILK PROCESSED USING THE METHOD

Technical field

The present invention relates to a method of controlling off flavor in raw milk and pasteurized milk, and to pasteurized milk processed using the controlling method.

To be more specific, the present invention relates to a method of controlling off flavor (abnormal flavor) in raw milk and pasteurized milk by controlling so-called spontaneous oxidized flavor caused by spontaneous oxidation of raw milk which is also called beany flavor (or cardboard flavor), controlling generation and/or increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, controlling cooked flavor which is problematic in quality and flavor of pasteurized milk or controlling generation and/or increase of sulfides which are believed to be causative substances of cooked flavor. The present invention also relates to pasteurized milk processed by using the off flavor controlling method.

In the present invention, the term "raw milk" implies milk fluids which are obtainable by subjecting fresh milk or crude milk to a cooling treatment or heating treatment to such a degree that quality and flavor thereof is not influenced, as well as fresh milk (raw milk before pasteurization) including crude milk (raw milk freshly milked from cow).

Further, in the present invention, the term "pasteurized milk" implies all milk fluids that are obtained by pasteurization of fresh milk or crude milk of mammals, as well as pasteurized raw milk.

Further, in the present invention, the wordings "immediately after milking" implies points of time up to three hours after milking as well as the point of time at which milking is conducted. In other words, "immediately after milking" also involves the time required for collecting milked crude milk into a tank or the like in a farm, and uniformizing the composition, for example, by stirring the collected crude milk. In general, milked crude milk is cooled to a temperature of about 5°C immediately, and this requires about two hours.

Background art

Off flavor of raw milk impairs good impressions (images) such as "naturalness", "deliciousness" and "nutrition/function" associated with milk. This may result in contraction in consumption of milk and eventually give an adverse affect on dairy industry.

Typical off flavors which are problematic in quality and flavor of raw milk include so-called spontaneous oxidized flavor which is caused by spontaneous oxidation of raw milk. Spontaneous oxidized flavor includes beany flavor (also referred to as cardboard flavor), cappy flavor, metallic flavor, tallowy flavor, oily flavor, fishy flavor and the like.

Details of mechanism for generation of spontaneous oxidized flavor has not been known, however, previous examinations have proved that carbonyl compounds such as hexanal are typical causative substances.

Spontaneous oxidized flavor is generated with time during refrigeration storage even in raw milk which is in good hygienic management and has no bacterial abnormality in quality. In such an occasion, carbonyl compounds such as hexanal in raw milk increase.

This spontaneous oxidized flavor may exert great influence on flavor of pasteurized milk, and hence quality management of raw milk is very important.

On the other hand, typical off flavors which are problematic in quality and flavor of pasteurized milk include cooked flavor, as well as the aforementioned beany flavor, generation of carbonyl compounds such as hexanal.

Typical causative substances of cooked flavor are believed to be sulfides. Sulfides are sulfur compounds such as dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS), for example.

In quality management of raw milk, when spontaneous oxidized flavor is found in a receiving stage at a milk processing plant after a certain lapse of time after milking of the crude milk, the raw milk will be repelled from acceptance.

On the other hand, when spontaneous oxidized flavor is found after pasteurization in a milk processing plant, shipping of products (pasteurized milk and the like) must be stopped.

In either case, products such as raw milk and pasteurized milk in which

spontaneous oxidized flavor is found will lose their industrial values and no longer be available as foods. This will lead to loss of agricultural resources. In other words, stable supply of milk with good quality and flavor by preventing or controlling off flavor of raw milk and pasteurized milk allows efficient use of agricultural resources without waste.

Therefore, it has been an important matter to be investigated in the dairy industry to clarify the mechanism in which off flavor is generated and to find a solution for preventing generation of such off flavor in raw milk and pasteurized milk.

However, no satisfactory solution has been suggested for off flavor, namely spontaneous oxidized flavor which is called beany flavor as described above, and cooked flavor in raw milk and pasteurized milk. For example, no satisfactory solution has been suggested for controlling generation of carbonyl compound such as hexanal and sulfides which are believed to be causative substances of beany flavor and cooked flavor.

If one can stably provide raw milk or pasteurized milk which is free of beany flavor and cooked flavor and thus are industrially valuable, by thoroughly conducting quality management of raw milk and pasteurized milk, it will promote customer's desire to purchase milk.

In order to achieve this, it is necessary to control off flavor in raw milk and pasteurized milk, namely, to control so-called spontaneous oxidized flavor caused by spontaneous oxidation of raw milk which is also called beany flavor, to control generation of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, to control cooked flavor which is problematic in quality and flavor of pasteurized milk or to control generation of sulfides which are believed to be causative substances of cooked flavor.

Conventional arts concerning milk with good quality and flavor and production methods thereof can be found in proposals of Japanese Patent Application Laid-Open Nos. 05-049395, 10-295341, 2001-078665, 2003-144045 and so on published from Japanese Patent Office.

Japanese Patent Application Laid-Open No. 05-049395 discloses a method of keeping freshness and preventing proliferation of bacteria by aerating (bubbling) stock fresh milk in a receptor tank prior to pasteurization with inert gas (nitrogen gas) to

achieve deoxidization.

Although it describes the condition in a tank (receptor tank) after acceptance at a plant in a step of subjecting milk to deoxidization, it fails to describe conditions during milking in farm therebefore and conditions in the receptor tank thereafter.

That is, temporal concept in the course from milking to pasteurization is not taken into account. The time lapse from milking of fresh milk in a farm to reception at a plant is typically two or three days. Further, fresh milk is sometimes transported long distance from the site of milking to a milk processing plant. For example, fresh milk milked in Hokkaido in Japan is sometimes transported such a long distance as to e.g., Japan's main island, where a milk processing plant is located.

As described above, carbonyl compound such as hexanal which are typical causative substances of spontaneous oxidized flavor, a typical off flavor which is problematic in quality and flavor of fresh milk will increase with time during refrigeration storage even in fresh milk which is in good hygienic management and has no bacterial abnormality in quality.

Hence, deoxidization after acceptance at plant may not sufficiently control the spontaneous oxidized flavor.

Therefore, thorough quality management in early stages after milking is crucial to produce milk with excellent quality and flavor.

Japanese Patent Application Laid-Open Nos. 10-295341 and 2001-078665 disclose methods of producing milk with excellent flavor by deoxidizing fresh milk under aeration with inert gas (nitrogen gas) followed by pasteurization. Although they describe flavor of milk after pasteurization, they fail to describe quality and flavor of fresh milk before pasteurization.

Japanese Patent Application Laid-Open No. 2003-1440345 discloses a method of producing milk with excellent flavor by packing pasteurized storage milk in a sterile tank in a package having oxygen barrier property in inert gas (nitrogen gas) atmosphere. Although it describes flavor of milk right before packed into a container (after pasteurization), it fails to describe quality and flavor of raw milk before pasteurization.

Disclosure of the Invention

Problems to be Solved by the Invention

The present invention was devised in consideration of the above problems of conventional arts, and it is an object of the present invention to provide a method of controlling off flavor in raw milk and pasteurized milk and to provide pasteurized milk processed by the controlling method.

More specifically, the present invention aims at proposing a method of controlling off flavor in raw milk and pasteurized milk by controlling so-called spontaneous oxidized flavor caused by spontaneous oxidation of raw milk which is also called beany flavor, controlling generation and/or increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, controlling cooked flavor which is problematic in quality and flavor of pasteurized milk or controlling generation and/or increase of sulfides which are believed to be causative substances of cooked flavor.

The present invention also aims at providing pasteurized milk which is processed by using the off flavor controlling method and available in production of milk with excellent quality and flavor.

Therefore, it is an ultimate object of the present invention to effectively utilize agricultural resources without waste by stably providing industrially available raw milk and pasteurized milk with little spontaneous oxidized flavor, reducing rejection of acceptance or stopping of shipping of raw and pasteurized milk caused by spontaneous oxidized flavor, and promoting the consumer's desire to purchase milk.

Means for Solving the Problem

In consideration of the above objects, the inventors of the present application made diligent effort and found that dissolved oxygen concentration of raw milk is one of the factors that control spontaneous oxidized flavor and cooked flavor of pasteurized milk, in the course from milking of crude milk to pasteurization.

We also found that by controlling and managing this factor, it is possible to control so-called spontaneous oxidized flavor caused by spontaneous oxidation of raw milk which is also called beany flavor, control generation and/or increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, control cooked flavor which is problematic in quality and flavor of pasteurized milk or control generation and/or increase of sulfides which are

believed to be causative substances of cooked flavor. We finally found that off flavor in raw milk and pasteurized milk can be controlled and accomplished the present invention.

In order to find a factor that controls so-called spontaneous oxidized flavor caused by spontaneous oxidation of raw milk which is also called beany flavor in raw milk or pasteurized milk, generation and/or increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, or cooked flavor which is problematic in quality and flavor of pasteurized milk or generation and/or increase of sulfides which are believed to be causative substances of cooked flavor, we introduced temporal concept in respect of change in quality and flavor of raw milk or pasteurized milk.

Concretely, we experimentally investigated at which point of time from milking, the control or management of dissolved oxygen concentration for raw milk or pasteurized milk should be conducted in order to effectively control spontaneous oxidized flavor of raw milk or pasteurized milk, generation/increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, or cooked flavor or generation and/or increase of sulfides which are believed to be causative substances of cooked flavor.

The result showed that great effect of controlling spontaneous oxidized flavor of raw milk or pasteurized milk, generation/increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, or cooked flavor or generation and/or increase of sulfides which are believed to be causative substances of cooked flavor is achieved when control or management of dissolved oxygen concentration is conducted before expected reception time at plant, e.g., in 72 hours after milking, preferably from 48 hours to 72 hours from milking, more preferably in 48 hours from milking, further preferably 24 hours from milking.

This in turn demonstrates that spontaneous oxidized flavor of raw milk or pasteurized milk, generation/increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, or cooked flavor or generation and/or increase of sulfides which are believed to be causative substances of cooked flavor is most desirably controlled when control or management of dissolved oxygen concentration is conducted in early time after milking in the course from

milking of crude milk to pasteurization, for example, immediately after milking in farm.

Through the above experiment, we determined a numerical range of dissolved oxygen concentration of raw milk or pasteurized milk which is effective for controlling spontaneous oxidized flavor of raw milk or pasteurized milk, generation/increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, or cooked flavor or generation and/or increase of sulfides which are believed to be causative substances of cooked flavor.

That is, the present invention proposes a method of controlling off flavor in raw milk and pasteurized milk, which is featured by a treatment of reducing dissolved oxygen concentration conducted in the course from milking to pasteurization in a processing step of milk.

The treatment of reducing dissolved oxygen concentration is conducted in 72 hours after milking.

Then, after conducting the treatment of reducing dissolved oxygen concentration, the condition in which dissolved oxygen concentration is low is kept until pasteurization.

In the above method of controlling off flavor in raw milk and pasteurized milk of the present invention, control of off flavor is achieved by at least one of the following controls.

- (1) Control of spontaneous oxidized flavor in raw milk;
- (2) Control of generation and/or increase of hexanal;
- (3) Control of cooked flavor; and
- (4) Control of generation and/or increase of sulfides.

In the above, the control of spontaneous oxidized flavor in raw milk is, for example, control of beany flavor.

The sulfides whose generation and/or increase is controlled in the above is at least one selected from the group consisting of dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS).

Next, the pasteurized milk proposed by the present invention is processed by using the method of controlling off flavor in raw milk and pasteurized milk of the present invention as described above.

Effect of the Invention

According to the present invention, it is possible to control so-called spontaneous oxidized flavor caused by spontaneous oxidation of raw milk which is also called beany flavor, generation and/or increase of carbonyl compounds such as hexanal which are believed to be causative substances of spontaneous oxidized flavor, cooked flavor which is problematic in quality and flavor of pasteurized milk or generation and/or increase of sulfides which are believed to be causative substances of cooked flavor, thereby controlling off flavor in raw milk and pasteurized milk.

Accordingly, it is possible to provide pasteurized milk which is processed by the method of controlling off flavor and applicable in production of milk with excellent quality and flavor.

As a result, it is possible to effectively utilize agricultural resources without waste by stably providing industrially available raw milk and pasteurized milk with little spontaneous oxidized flavor, reducing rejection of acceptance or stop of shipping of the raw and pasteurized milk caused by spontaneous oxidized flavor, and promoting the consumer's desire to purchase milk.

Best Mode for Carrying Out the Invention

A method of controlling off flavor in raw milk and pasteurized milk of the present invention involves a treatment of reducing dissolved oxygen concentration in the course from milking to pasteurization in the processing step of milk.

Here, the treatment of reducing dissolved oxygen concentration is preferably conducted in 72 hours after milking.

Further, after conducting the treatment of reducing dissolved oxygen concentration, it is preferred to keep the condition in which dissolved oxygen concentration is low until pasteurization.

The control of off flavor in the above description is achieved by at least one of the following controls.

- (1) Control of spontaneous oxidized flavor in raw milk;
- (2) Control of generation and/or increase of hexanal;
- (3) Control of cooked flavor; and
- (4) Control of generation and/or increase of sulfides.

In the above, the control of spontaneous oxidized flavor in raw milk is for example, control of beany flavor, and the sulfides whose generation and/or increase is controlled in the above is at least one selected from the group consisting of dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS).

In the experiment made by the present inventors, any of spontaneous oxidized flavor in raw milk, generation and/or increase of hexanal, cooked flavor and generation and/or increase of sulfides are controlled in the raw milk subjected to the treatment of reducing dissolved oxygen concentration.

Therefore, by conducting the treatment of reducing dissolved oxygen concentration of raw milk, it is possible to execute any of control of spontaneous oxidized flavor in raw milk, control of generation and/or increase of hexanal, control of cooked flavor and control of generation and/or increase of sulfides which are employed for controlling off flavor in raw milk and pasteurized milk.

In the method of controlling off flavor in raw milk and pasteurized milk according to the present invention, the treatment of reducing dissolved oxygen concentration can be principally conducted at any point of time in the course between milking and pasteurization.

The course between milking and pasteurization involves the following steps: (1) milking from cow; (2) storage in a milk collecting tank in a farm (tank installed in farm); (3) transfer from a milk collecting tank in farm to tanker (vehicle, marine vessel, aircraft); (4) transport by a tanker; and (5) transfer from a tanker to a milk processing plant, and so on.

Although some of the aforementioned steps between milking to acceptance to plant are sometimes omitted, the treatment of reducing dissolved oxygen concentration may principally be conducted at any of these steps.

Therefore, the treatment of reducing dissolved oxygen concentration of raw milk can be conducted in any of the instruments, tools, and apparatuses described below.

- (A) in a hosepipe or in a pipe used for milking from cow;
- (B) in a tank installed in a farm for collecting milk (milk collecting tank);
- (C) in a hosepipe or in a pipe for transferring fresh milk from a milk collecting tank to a tanker for transporting fresh milk;

(D) in a tank of tanker; and

(E) in a hosepipe or in a pipe for transferring fresh milk from a tanker to a milk processing plant.

From the viewpoint of stably ensuring pasteurized milk with excellent quality and flavor, it is preferred that the treatment of reducing dissolved oxygen concentration of raw milk is conducted in a short time after milking.

When the dissolved oxygen concentration of raw milk is reduced in a short time after milking, the effect of controlling deterioration in quality and flavor of raw milk is improved, so that the quality and flavor of pasteurized milk that is obtained by pasteurization of such raw milk is advantageously improved.

When the treatment of reducing dissolved oxygen concentration is conducted immediately after milking in a farm, any of spontaneous oxidized flavor in raw milk, generation and/or increase of hexanal, cooked flavor, and generation and/or increase of sulfides are controlled, and it is possible to maximally exert the effect of controlling off flavor in raw milk and pasteurized milk.

Since about 72 hours is required before acceptance at a plant after milking, the aforementioned effect can be exerted by conducting the treatment of reducing dissolved oxygen concentration of raw milk at the time of milking or in 72 hours after milking.

It is desired to conduct the treatment of reducing dissolved oxygen concentration of raw milk in shorter time after milking for the purpose of best exertion of the effect of controlling off flavor in raw milk and pasteurized milk by controlling any of spontaneous oxidized flavor in raw milk, generation and/or increase of hexanal, cooked flavor, and generation and/or increase of sulfides. It is preferred that the treatment of reducing dissolved oxygen concentration of raw milk is conducted in 72 hours, preferably in 48 hours, more preferably in 24 hours from milking, and most preferably immediately after milking.

The method of reducing dissolved oxygen concentration of raw milk is not particularly limited. For example, degassing in vacuum atmosphere or displacing oxygen with inert gas and the like techniques may be used. In the technique of displacing oxygen with inert gas, use of aeration (bubbling) of inert gas eliminates the necessity of a complicated apparatus. When oxygen is displaced by inert gas, nitrogen gas may be used as the inert gas. Nitrogen gas is easy to handle and inexpensive.

In the above description, the numerical range of dissolved oxygen concentration at the time when the treatment of reducing dissolved oxygen concentration of raw milk is executed is not particularly limited, however lower dissolved oxygen concentration of raw milk is preferred from the viewpoint of improvement of the effect of controlling deterioration in quality and flavor of raw milk.

According to the experiment conducted by the present inventors, in order to control the spontaneous oxidized flavor of any raw milk that is empirically susceptible to spontaneous oxidation (poor quality) and to control generation of hexanal, it is necessary to control the dissolved oxygen concentration of raw milk to 2 ppm or less.

On the other hand, in order to control the spontaneous oxidized flavor of any raw milk that is empirically insusceptible to spontaneous oxidation (good quality) and to control generation of hexanal, 5 ppm of dissolved oxygen concentration of raw milk suffices and provides a comparable effect of controlling generation of hexanal with that realized by concentration of 2 ppm or less.

In other words, a preferred numerical range of dissolved oxygen concentration at the time of execution of the treatment of reducing dissolved oxygen concentration of raw milk is influenced by the quality of raw milk, such as insusceptibility to spontaneous oxidation (good quality) and susceptibility to spontaneous oxidation (poor quality).

The quality of raw milk is influenced by breeding condition (feed, land etc.) of cow, and seasonal variations.

In general, raw milk is managed in good quality condition (resistant to spontaneous oxidation). Therefore, even when the dissolved oxygen concentration at the time of execution of the treatment of reducing dissolved oxygen concentration of raw milk is 5 ppm, any of the spontaneous oxidized flavor in raw milk, generation and/or increase of hexanal, cooked flavor and generation and/or increase of sulfides are controlled, and the effect of controlling off flavor in raw milk and pasteurized milk can be exerted.

Even if raw milk is in such an environment that is more or less likely to generate off flavor, when the dissolved oxygen concentration at the time of execution of the treatment of reducing dissolved oxygen concentration of raw milk is lower, any of the spontaneous oxidized flavor in raw milk, generation and/or increase of hexanal,

cooked flavor and generation and/or increase of sulfides are controlled, and the effect of controlling off flavor in raw milk and pasteurized milk is exerted more effectively.

The dissolved oxygen concentration at the time of execution of the treatment of reducing dissolved oxygen concentration of raw milk is preferably 4 ppm or less, more preferably 3 ppm or less, and further preferably 2 ppm or less.

In the method of controlling off flavor in raw milk and pasteurized milk according to the present invention, after conducting the treatment of reducing dissolved oxygen concentration described above, it is desired to keep the condition in which dissolved oxygen concentration is low until pasteurization. Here, the condition in which dissolved oxygen concentration is low may be kept, for example, by preventing contact with oxygen.

Even after reducing dissolved oxygen concentration of raw milk, by keeping the dissolved oxygen concentration of raw milk at low level, the effect of controlling deterioration in quality and flavor of raw milk is improved, and accordingly quality and flavor of pasteurized milk that is obtained by pasteurizing the raw milk are improved. Further, even after reducing dissolved oxygen concentration of raw milk, by keeping the dissolved oxygen concentration of raw milk at low level, it is possible to stably ensure raw milk with excellent quality and flavor.

As described above, the treatment of reducing dissolved oxygen concentration of raw milk may be conducted, for example, in a hosepipe or in a pipe used for milking from cow; in a tank installed in a farm for collecting milk (milk collecting tank); in a hosepipe or in a pipe for transferring fresh milk from a milk collecting tank to a tanker for transporting fresh milk; in a tank of a tanker; or in a hosepipe or in a pipe for transferring fresh milk from a tanker to a milk processing plant.

In order to keep the dissolved oxygen concentration of raw milk at low after execution of the treatment of reducing dissolved oxygen concentration of raw milk, it is preferred that the management for keeping the dissolved oxygen concentration of raw milk at low level is conducted in all instruments, tools, apparatuses and steps provided before pasteurization step in plant after the above exemplified instruments, tools and apparatus in which the treatment of reducing dissolved oxygen concentration is executed.

In this case, it is important to control and manage dissolved oxygen

concentration of raw milk in a tank and a pump. Accordingly, some measure should be taken such as creating nitrogen atmosphere in a tank or introducing a liquid feeding pump into a container which is somewhat hermetic to create nitrogen atmosphere in the interior of the container.

As described above, the method of controlling off flavor in raw milk and pasteurized milk according to the present invention is characterized by conducting the treatment of reducing dissolved oxygen concentration immediately after milking or at a certain point of time after milking, and by subsequently keeping the condition in which dissolved oxygen concentration is low as is necessary.

In the present invention, we examined the effect of controlling off flavor in raw milk and pasteurized milk based on the sensory evaluation about spontaneous oxidized flavor (beany flavor) or cooked flavor in raw milk and concentration of hexanal and sulfides as index.

The method of the present invention provides effects which are industrially revolutionary, as preventing generation of off flavor and preventing loss of commercial value, as well as improving flavor of pasteurized milk. In other words, the present invention differs from conventional art in that not only is flavor improved, but also deterioration of quality is prevented. It also differs from conventional arts in that time concept is introduced for the period between milking and pasteurization.

The present invention will now be explained by way of examples, but the present invention is not limited to these examples.

In Examples 1-3, 5 and 7-9, raw milk (fresh milk) which is susceptible to spontaneous oxidation was used. On the other hand, in Examples 4 and 6, raw milk (fresh milk) which is insusceptible to spontaneous oxidation was used. In Examples 1-4 and 7-8, a technique of displacing oxygen with inert gas was used for reducing dissolved oxygen concentration. On the other hand, in Examples 5, 6 and 9, a technique of degassing in vacuum atmosphere was used for reducing dissolved oxygen concentration.

Example 1

(Temporal changes in beany flavor and hexanal concentration when dissolved oxygen concentration was reduced immediately after milking, and retained in an open container

and retained in a hermetic container)

Temporal changes in beany flavor and hexanal concentration were examined when dissolved oxygen concentration was reduced immediately after milking, and retained in an open container or in a hermetic container.

Over about 30 minutes after milking, the temperature of crude milk was cooled to 8°C. At this time the dissolved oxygen concentration of crude milk was 9.6 ppm (temperature: 8°C). The crude milk for which the dissolved oxygen concentration was not adjusted was used as a reference sample (control) in the name of "unadjusted raw milk".

Immediately after milking, the unadjusted raw milk was aerated with nitrogen gas, and the dissolved oxygen concentration was lowered to 0.8 ppm (temperature 7°C).

The raw milk for which dissolved oxygen concentration was adjusted was charged into two types of containers: a plastic bottle having poor gas barrier property (polyethylene container, which is called "open container"); and a steel can container having excellent gas barrier property (which is called "hermetic container"). These are respectively named "raw milk of low oxygen in open condition" and "raw milk of low oxygen in hermetic condition".

Dissolved oxygen concentration, beany flavor and hexanal concentration were compared among unadjusted raw milk, raw milk of low oxygen in open condition, and raw milk of low oxygen in hermetic condition, and the results are shown in Figs. 1 to 3.

In this case, the raw milk was stored for several days at a temperature of 2°C in dark. Also in the following examples, the condition for storage of raw milk for several days was a temperature of 2°C in dark.

Fig. 1 shows temporal changes of dissolved oxygen concentration for unadjusted raw milk, raw milk of low oxygen in open condition, and raw milk of low oxygen in hermetic condition.

Dissolved oxygen concentration was measured with a portable DO meter DO-21P (DKK-TOA Corporation).

Since measurements of dissolved oxygen concentration are somewhat instable depending on the measurement condition, measurement was conducted in the following manner: (1) fluid (raw milk) to be measured was stirred with a stirrer, and the flow rate was adjusted at 10 cm/sec or more; and (2) an electrode of the DO meter was put into

the stirred raw milk, and a stabilized numerical value was read after about 3 minutes. In this manner, reliable measurement was obtained.

Dissolved oxygen concentration of unadjusted raw milk transited at high level.

Dissolved oxygen concentration of raw milk of low oxygen in open condition reached a numerical value which is comparable to that of unadjusted raw milk after a lapse of 24 hours from milking.

Dissolved oxygen concentration of raw milk of low oxygen in hermetic condition transited at such a low level that is identical to that immediately after adjustment.

These results demonstrate that placing in hermetic condition after adjusting the dissolved oxygen concentration at low level is effective for keeping the dissolved oxygen concentration of raw milk at low level.

As a measure for keeping the dissolved oxygen concentration at low level, keeping the raw milk in an inert gas (e.g., nitrogen gas) atmosphere is conceived as well as placing in hermetic condition.

Fig. 2 shows temporal changes of beany flavor for unadjusted raw milk, raw milk of low oxygen in open condition, and raw milk of low oxygen in hermetic condition.

Sensory evaluation of beany flavor was carried out by 7-ranked evaluation by five special panelists as follows: 0 point (not sensed), 0.5 point (little sensed), 1 point (slightly sensed), 1.5 point (partly sensed), 2 points (sensed), 2.5 points (clearly sensed), and 3 points (strongly sensed), and average values were compared for each condition.

Beany flavor of unadjusted raw milk was zero immediately after milking, and all special panelists completely failed to sense beany flavor; however, after a lapse of 12 hours from milking, the evaluation was 0.4, showing that beany flavor was partly sensed. The beany flavor still increased thereafter, and the evaluation reached 3 after 72 hours where all special panelists strongly sensed the beany flavor.

Beany flavor of raw milk of low oxygen in open condition was zero after a lapse of 12 hours from milking, and all special panelists completely failed to sense beany flavor, but after a lapse of 24 hours from milking, the evaluation was 0.9, showing that beany flavor was partly sensed. The beany flavor still increased thereafter, and reached a numerical value which is identical to that of unadjusted raw

milk after a lapse of 72 hours from milking.

As to the raw milk of low oxygen in open condition, the time from which beany flavor begins to be sensed was delayed compared to unprocessed raw milk.

Beany flavor of raw milk of low oxygen in hermetic condition was zero after a lapse of 12 hours from milking, and all special panelists completely failed to sense beany flavor, but after a lapse of 24 hours from milking, the evaluation was 0.4, showing that beany flavor was partly sensed. The beany flavor slightly increased thereafter, however even after a lapse of 72 hours, it was merely slightly sensed such that the evaluation was 1.0.

As described above, beany flavor of the raw milk of low oxygen in hermetic condition transited at low numerical level. Placing in hermetic condition after adjusting the dissolved oxygen concentration at low level is effective for preventing and controlling beany flavor of raw milk.

Even when the raw milk is placed in open condition after adjusting the dissolved oxygen concentration at low level, the effect of controlling beany flavor lasted up to 24 hours after milking. However, after a lapse of 48 hours from adjustment, the numerical value was comparable to that of unadjusted raw milk and the effect of controlling beany flavor was lost.

Fig. 3 shows temporal changes of hexanal concentration for unadjusted raw milk, raw milk of low oxygen in open condition, and raw milk of low oxygen in hermetic condition.

Hexanal concentration was measured according to the solid-phase micro extraction (SPME method) as described below. Concretely: (1) collect a sample (capacity: 10 mL (milliliters)) in a vial container (capacity: 20 mL), add methylisobutylketone (MIBK) as an internal standard substance and hermetically seal the vial container; (2) heat the vial container at 60°C for a retention time of 40 minutes; (3) extract "odor component" present in the head space of the vial container with solid-phase microextraction (SPME) (85 μ m Stable Flex Carboxen/PDMS); (4) analyze by GC/MS (column: CP-WAX); and (5) add a standard preparation of hexanal to milk and create an analytical curve which is standardized based on the internal standard substance in order to quantify hexanal concentration.

Although the solid-phase micro extraction method (SPME method) allows

rapid analysis of volatile "flavor component" with high sensitivity, the quantitative ability was viewed with suspicion. According to the present method, a rapid quantification analysis is realized.

Hexanal concentration of unadjusted raw milk was 1 $\mu\text{g/L}$ (micrograms/litter) immediately after milking, 5 $\mu\text{g/L}$ after a lapse of 12 hours from milking, and 10 $\mu\text{g/L}$ or more after a lapse of 24 hours from milking. The hexanal concentration still continued to increase thereafter and reached 20 $\mu\text{g/L}$ or more after a lapse of 48 hours.

Hexanal concentration of raw milk of low oxygen in open condition was 3 $\mu\text{g/L}$ (micrograms/litter) after a lapse of 12 hours from milking, and 10 $\mu\text{g/L}$ after a lapse of 24 hours from milking. Thereafter, the hexanal concentration increased and reached the numerical value which was comparable to that of unadjusted raw milk after a lapse of 48 hours.

In hexanal concentration of raw milk of low oxygen in open condition, however, the time at which hexanal concentration begins to increase was delayed compared to the case of unadjusted raw milk.

Hexanal concentration of raw milk of low oxygen in hermetic condition was as low as 1 $\mu\text{g/L}$ even after a lapse of 12 hours from milking, which was comparable to that immediately after milking. Even after a lapse of 72 hours from milking, the numerical value was 2 $\mu\text{g/L}$, and hexanal concentration of raw milk of low oxygen in hermetic condition little changed and transited in low numerical values.

It was found that keeping hermetic condition after adjusting the dissolved oxygen concentration at low level is effective for keeping the hexanal concentration of raw milk at low level.

Even when the raw milk is placed in open condition after adjusting the dissolved oxygen concentration at low level, the effect of controlling increase in hexanal concentration lasted until 24 hours after milking. However, after a lapse of 48 hours from adjustment, the numerical value was comparable to that of unadjusted raw milk and the effect of controlling increase in hexanal concentration was lost.

From the comparison between Figs. 2 and 3, the correlation between beany flavor and hexanal concentration was reaffirmed.

In the following Examples, only hexanal concentration was evaluated, and evaluation of beany flavor was omitted.

Example 2

(Temporal changes of hexanal concentration for cases where dissolved oxygen concentration was decreased immediately after milking, after a lapse of 24 hours from milking and after a lapse of 48 hours from milking)

Temporal changes of hexanal concentration for cases where dissolved oxygen concentration was decreased immediately after milking, after a lapse of 24 hours from milking and after a lapse of 48 hours from milking were examined.

Over about 30 minutes after milking, the temperature of crude milk was cooled to 8°C. At this time the dissolved oxygen concentration of crude milk was 9.6 ppm (temperature: 8°C). The crude milk for which the dissolved oxygen concentration was not adjusted was used as a reference sample (control) in the name of "unadjusted raw milk".

Three different lapse times: immediately after milking, after a lapse of 24 hours from milking and after a lapse of 48 hours from milking were selected regarding the time at which dissolved oxygen concentration was decreased after milking.

Immediately after milking, after a lapse of 24 hours from milking and after a lapse of 48 hours from milking, respectively, unadjusted raw milk was aerated with nitrogen gas, the dissolved oxygen concentration was reduced to 0.8 ppm (at 7°C), and the milk was charged into a steel can container (which is called "hermetic container") having good gas barrier property. These samples were respectively named "raw milk of low oxygen immediately after milking", "raw milk of low oxygen after a lapse of 24 hours from milking" and "raw milk of low oxygen after a lapse of 48 hours from milking".

Fig. 4 shows results of comparison of dissolved oxygen concentration for unadjusted raw milk, raw milk of low oxygen immediately after milking, raw milk of low oxygen after a lapse of 24 hours from milking and raw milk of low oxygen after a lapse of 48 hours from milking.

Temporal changes of dissolved oxygen concentration for unadjusted raw milk, raw milk of low oxygen immediately after milking, raw milk of low oxygen after a lapse of 24 hours from milking and raw milk of low oxygen after a lapse of 48 hours from milking were measured by the method described in Example 1.

Dissolved oxygen concentration of unadjusted raw milk transited at high level.

Dissolved oxygen concentration of raw milk of low oxygen immediately after milking transited at such a low level as comparable to that of immediately after adjustment.

As to the raw milk of low oxygen after a lapse of 24 hours from milking and raw milk of low oxygen after a lapse of 48 hours from milking, dissolved oxygen concentrations were kept at such a high level as comparable to that of unadjusted raw milk until adjustment, however, they transited at low level after adjustment.

It was reaffirmed that bringing into hermetic condition after adjusting the dissolved oxygen concentration low is effective for keeping the dissolved oxygen concentration of raw milk at low level.

As described above, as a measure for keeping the dissolved oxygen concentration at low level, keeping the raw milk in an inert gas (e.g., nitrogen gas) atmosphere is conceived as well as placing in hermetic condition.

Fig. 5 shows temporal changes of hexanal concentration for unadjusted raw milk, raw milk of low oxygen immediately after milking, raw milk of low oxygen after a lapse of 24 hours from milking, and raw milk of low oxygen after a lapse of 48 hours from milking.

Hexanal concentration was measured according to the method described in Example 1.

Hexanal concentration of unadjusted raw milk was 1 $\mu\text{g/L}$ immediately after milking, 5 $\mu\text{g/L}$ after a lapse of 12 hours from milking, and 10 $\mu\text{g/L}$ or more after a lapse of 24 hours from milking. The hexanal concentration still continued to increase thereafter and reached 20 $\mu\text{g/L}$ or more after a lapse of 48 hours.

Hexanal concentration of raw milk of low oxygen immediately after milking was as low as 1 $\mu\text{g/L}$ even after a lapse of 12 hours from milking, which was comparable to that of immediately after milking. Hexanal concentration of raw milk of low oxygen immediately after milking little changed and transited at low level as was 2 $\mu\text{g/L}$ even after a lapse of 72 hours from milking.

Hexanal concentrations of raw milk of low oxygen after a lapse of 24 hours from milking, and raw milk of low oxygen after a lapse of 48 hours from milking were at such high levels as comparable with that of unadjusted raw milk before adjustment,

however, they remained unchanged or decreased to a certain degree after adjustment.

Not only immediately after milking, but also after a lapse of 24 hours from milking and after a lapse of 48 hours from milking, increase in hexanal concentration was stopped when the dissolved oxygen concentration was adjusted at low level. It in turn demonstrates that spontaneous oxidation is stopped when the dissolved oxygen concentration is adjusted at low level.

The earlier the timing at which the dissolved oxygen concentration of raw milk is adjusted at low level, the greater the effect of controlling spontaneous oxidized flavor is, however, it was found that the effect of controlling spontaneous oxidized flavor is realized to a certain degree by adjusting the dissolved oxygen concentration at low level before the spontaneous oxidation reaction comes into saturated state.

It was reaffirmed that keeping in hermetic condition after adjusting the dissolved oxygen concentration at low level is effective for keeping the hexanal concentration of raw milk at low level.

Example 3

(Temporal change of hexanal concentration when dissolved oxygen concentration of raw milk which is susceptible to spontaneous oxidation is changed by a method of displacing oxygen with inert gas)

Temporal change of hexanal concentration when dissolved oxygen concentration of raw milk which was susceptible to spontaneous oxidation was changed immediately after milking was examined.

For reducing dissolved oxygen concentration, a method of displacing oxygen with inert gas was used.

Over about 30 minutes after milking, the temperature of crude milk was cooled to 8°C. At this time the dissolved oxygen concentration of crude milk was 9.6 ppm (temperature: 8°C).

The crude milk for which the dissolved oxygen concentration was not adjusted was used as a reference sample (control) in the name of "unadjusted raw milk".

At the end of milking, two levels of dissolved oxygen concentration: 0.8 ppm and 4.8 ppm (temperature 7°C) were selected.

Specifically, immediately after milking, unadjusted raw milk was aerated with

nitrogen gas and the dissolved oxygen concentration was reduced to the above levels, and the milk was charged into a steel can container (called "hermetic container") having good gas barrier property. These samples were respectively named "raw milk of low oxygen-0.8 ppm", and "raw milk of low oxygen-4.8 ppm".

Figs. 6 and 7 show comparison results of dissolved oxygen concentration and hexanal concentration between unadjusted raw milk, and raw milk of low oxygen-0.8 ppm.

Fig. 6 shows temporal change of dissolved oxygen concentration for unadjusted raw milk and raw milk of low oxygen-0.8 ppm.

Dissolved oxygen concentration was measured by the method described in Example 1.

Dissolved oxygen concentration of unadjusted raw milk transited at high level.

Dissolved oxygen concentration of low oxygen-4.8 ppm was comparable to that immediately after adjustment, and hence description thereof is omitted here.

Dissolved oxygen concentration of low oxygen-0.8 ppm transited at low level as comparable to that immediately after adjustment.

It was found that dissolved oxygen concentration may possibly be kept at low level and spontaneous oxidation reaction of raw milk may possibly be stopped when hermetic condition is established after adjusting the dissolved oxygen concentration at such low level about 1 ppm.

Fig. 7 shows temporal change of hexanal concentration for unadjusted raw milk and raw milk of low oxygen-0.8 ppm.

Hexanal concentration was measured according to the method described in Example 1.

Hexanal concentration of unadjusted raw milk was 1 $\mu\text{g/L}$ immediately after milking, 5 $\mu\text{g/L}$ after a lapse of 12 hours from milking, and 10 $\mu\text{g/L}$ or more after a lapse of 24 hours from milking. The hexanal concentration still continued to increase thereafter and reached 20 $\mu\text{g/L}$ or more after a lapse of 48 hours.

Hexanal concentration of raw milk of low oxygen-4.8 ppm reached the numerical value which was comparable to that of unadjusted raw milk after a lapse of 24 hours from milking, and increased at a level comparable to that of unadjusted raw milk, and hence description thereof is omitted here.

Hexanal concentration of raw milk of low oxygen-0.8 ppm was 2 µg/L even after a lapse of 72 hours from milking and transited at a level similar to that of immediately after milking.

Hexanal concentration stopped increasing when dissolved oxygen concentration was adjusted at such low level as 1 ppm or less. In other words, by adjusting the dissolved oxygen concentration at such low level as 1 ppm or less, spontaneous oxidation was stopped.

The lower the dissolved oxygen concentration of raw milk is adjusted, the greater the effect of controlling spontaneous oxidized flavor is.

In this example, since raw milk which was susceptible to spontaneous oxidation was used, it was necessary to make the dissolved oxygen concentration of raw milk 1 ppm or less in order to control spontaneous oxidized flavor and generation of hexanal.

In contrast, when raw milk which was insusceptible to spontaneous oxidation was used in the experiment as described in Example 4 below, 5 ppm of dissolved oxygen concentration of raw milk sufficed for controlling spontaneous oxidized flavor or generation of hexanal. In the case of raw milk which is believed to be insusceptible to spontaneous oxidation, effect of controlling generation of hexanal which was comparable to that realized by dissolved oxygen concentration of raw milk of 2 ppm or less was obtained when the dissolved oxygen concentration of raw milk was adjusted to 5 ppm.

In other words, the condition required for dissolved oxygen concentration or the like is influenced by quality of raw milk.

The quality of raw milk is influenced by breeding condition (feed, land etc.) of cow, and seasonal variations. In general, since quality of raw milk is managed in good conditions and hence insusceptible to spontaneous oxidation, an effect of controlling spontaneous oxidized flavor is realized even when the dissolved oxygen concentration is adjusted at 5 ppm.

Example 4

(Temporal change of hexanal concentration when dissolved oxygen concentration of raw milk which was insusceptible to spontaneous oxidation was changed by a method

of displacing oxygen with inert gas)

Temporal change of hexanal concentration when dissolved oxygen concentration of raw milk which was insusceptible to spontaneous oxidation was changed after 24 hours from milking was examined.

For reducing dissolved oxygen concentration, a method of displacing oxygen with inert gas was used.

Over about 30 minutes after milking, the temperature of crude milk was cooled to 8°C. At this time the dissolved oxygen concentration of crude milk was 9.2 ppm (temperature: 8°C).

The crude milk for which the dissolved oxygen concentration was not adjusted was used as a reference sample (control) in the name of "unadjusted raw milk".

After a lapse of 24 hours from milking, two levels of dissolved oxygen concentration: 2.0 ppm and 5.0 ppm (temperature 7°C) were selected.

Specifically, after a lapse of 24 hours from milking, unadjusted raw milk was aerated with nitrogen gas and the dissolved oxygen concentration was reduced to the above levels, and the milk was charged into a steel can container (called "hermetic container") having good gas barrier property. These samples were respectively named "raw milk of low oxygen-2.0 ppm", and "raw milk of low oxygen-5.0 ppm".

Figs. 8 and 9 show comparison results of dissolved oxygen concentration and hexanal concentration among unadjusted raw milk, raw milk of low oxygen-2.0 ppm, and raw milk of low oxygen-5.0 ppm.

Fig. 8 shows temporal change of dissolved oxygen concentration for unadjusted raw milk, raw milk of low oxygen-2.0 ppm, and raw milk of low oxygen-5.0 ppm.

Dissolved oxygen concentration was measured by the method described in Example 1.

Dissolved oxygen concentration of unadjusted raw milk transited at high level.

Dissolved oxygen concentrations of raw milk of low oxygen-2.0 ppm, and of low oxygen-5.0 ppm transited at low level as comparable to that immediately after adjustment.

It was found that dissolved oxygen concentration may possibly be kept at low level and spontaneous oxidation reaction of raw milk may possibly be stopped when

hermetic condition is established after adjusting the dissolved oxygen concentration at such low level about 5 ppm.

Fig. 9 shows temporal change of hexanal concentration for unadjusted raw milk, raw milk of low oxygen-2.0 ppm, and raw milk of low oxygen-5.0 ppm.

Hexanal concentration was measured according to the method described in Example 1.

Hexanal concentration of unadjusted raw milk was 4 $\mu\text{g/L}$ at the start of experiment, 10 $\mu\text{g/L}$ after a lapse of 72 hours, and 12 $\mu\text{g/L}$ after a lapse of 96 hours. The hexanal concentration still continued to increase thereafter and reached 20 $\mu\text{g/L}$ after a lapse of 168 hours.

Hexanal concentrations of raw milk of low oxygen-2.0ppm, and raw milk of low oxygen-5.0ppm transited at such low levels as 6 or 8 $\mu\text{g/L}$, after a lapse of 72 hours.

When the dissolved oxygen concentration was adjusted at such low level as 5.0 ppm or less, increase in hexanal concentration was moderated.

In brief, when the dissolved oxygen concentration was adjusted at 5.0 ppm or less, spontaneous oxidation was controlled.

The lower the level at which the dissolved oxygen concentration of raw milk is adjusted, the greater the effect of controlling spontaneous oxidized flavor. In the case of raw milk which is insusceptible to spontaneous oxidation, the effect of controlling generation and increase of hexanal was observed even when the dissolved oxygen concentration of raw milk was adjusted at 5 ppm.

Example 5

(Temporal change of hexanal concentration when dissolved oxygen concentration of raw milk which was susceptible to spontaneous oxidation was changed by a method of degassing in vacuum atmosphere)

Temporal change of hexanal concentration was examined when dissolved oxygen concentration of raw milk which was susceptible to spontaneous oxidation was changed after a lapse of 24 hours from milking of raw milk.

In this Example, raw milk which was susceptible to spontaneous oxidation was prepared by adding copper ion to the raw milk at a final concentration of 1 ppm.

In order to lower dissolved oxygen concentration, a method of degassing in

vacuum atmosphere was used.

Over about 30 minutes after milking, temperature of crude milk was cooled to 8°C. Dissolved oxygen concentration of crude milk was 11.2 ppm (temperature 8°C).

Crude milk which was not subjected to adjustment of dissolved oxygen concentration was used as reference sample (control), which was named "unadjusted raw milk".

The method of degassing in vacuum atmosphere was conducted in the following manner. About 500 mL (milliliters) of unadjusted raw milk was put into a recovery flask (capacity: 1L (litter)) which was then attached to an evaporator. While ice-cooling the recovery flask, the interior of the flask was brought into a vacuum atmosphere (pressure 30 mmHg), and retained for 15 minutes. After that, the interior of the flask was opened to atmospheric pressure in nitrogen gas atmosphere so as to prevent rapid entry of air.

As a result of the above process, the dissolved oxygen concentration was adjusted at 2.1 ppm (temperature 7°C) after a lapse of 24 hours from milking.

This was then charged into a steel can (called "hermetic container") having excellent gas barrier property (which is named "raw milk of low oxygen (degassed)-2.1 ppm").

Comparison results of hexanal concentration between unadjusted raw milk, and raw milk of low oxygen (degassed)-2.1 ppm are shown in Fig. 10.

Fig. 10 shows temporal change of hexanal concentration for unadjusted raw milk, and raw milk of low oxygen (degassed)-2.1 ppm.

Hexanal concentration was measured by the method described in Example 1.

Hexanal concentration of unadjusted raw milk was 3 µg/L at the start of experiment and 14 µg/L after a lapse of 24 hours.

Hexanal concentration of raw milk of low oxygen (degassed)-2.1 ppm was as low as 5 µg/L even after a lapse of 24 hours.

When the dissolved oxygen concentration was adjusted at such low level as 2.1 ppm or less, increase in hexanal concentration was moderated.

That is, by adjusting the dissolved oxygen concentration at such low level as 2.1 ppm or less, the spontaneous oxidation was controlled.

These results taken together with the results of previous examples demonstrate

that spontaneous oxidation is controlled by reducing dissolved oxygen concentration of raw milk, regardless of the way in which dissolved oxygen concentration is reduced such as degassing in vacuum atmosphere and displacement of oxygen with inert gas.

In this example, since the raw milk which was susceptible to spontaneous oxidation is used in the experiment, it was necessary to adjust the dissolved oxygen concentration at 2.1 ppm or less for controlling spontaneous oxidized flavor and generation of hexanal.

In contrast, when raw milk which is insusceptible to spontaneous oxidation is used as described in Example 4, 5 ppm of dissolved oxygen concentration of raw milk suffices for controlling spontaneous oxidized flavor or generation of hexanal. In the case of raw milk which is insusceptible to spontaneous oxidation, effect of controlling generation of hexanal which is comparable to that realized by dissolved oxygen concentration of raw milk of 2 ppm or less was obtained when the dissolved oxygen concentration of raw milk was adjusted to 5 ppm.

In other words, the condition required for dissolved oxygen concentration or the like is influenced by quality of raw milk.

The quality of raw milk is influenced by breeding condition (feed, land etc.) of cow, and seasonal variations. In general, since quality of raw milk is managed in good conditions and hence insusceptible to spontaneous oxidation, an effect of controlling spontaneous oxidized flavor is realized even when the dissolved oxygen concentration is adjusted at 5 ppm.

Example 6

(Temporal change of hexanal concentration when dissolved oxygen concentration of raw milk which is insusceptible to spontaneous oxidation is changed by a method of degassing in vacuum atmosphere)

Temporal change of hexanal concentration was examined when dissolved oxygen concentration of raw milk which is insusceptible to spontaneous oxidation is changed after a lapse of 24 hours from milking of raw milk.

In order to lower dissolved oxygen concentration, a method of degassing in vacuum atmosphere was used.

Over about 30 minutes after milking, temperature of crude milk was cooled to

8°C. Dissolved oxygen concentration of crude milk was 11.2 ppm (temperature 8°C).

Crude milk which was not subjected to adjustment of dissolved oxygen concentration was used as reference sample (control) in the name of "unadjusted raw milk".

By the method of degassing in vacuum atmosphere as described in Example 5, dissolved oxygen concentration was adjusted at 2.1 ppm (temperature 7°C) after a lapse of 24 hours from milking.

This was then charged into a steel can (called "hermetic container") having excellent gas barrier property (which is named "raw milk of low oxygen (degassed)-2.1 ppm").

Comparison results of hexanal concentration between unadjusted raw milk, and raw milk of low oxygen (degassed)-2.1 ppm are shown in Fig. 11.

Fig. 11 shows temporal change of hexanal concentration for unadjusted raw milk, and raw milk of low oxygen (degassed)-2.1 ppm.

Hexanal concentration was measured by the method described in Example 1.

Hexanal concentration of unadjusted raw milk was 3 µg/L at the start of experiment and 7 µg/L after a lapse of 72 hours.

Hexanal concentration of raw milk of low oxygen (degassed)-2.1 ppm was as low as 4 µg/L even after a lapse of 72 hours.

When the dissolved oxygen concentration was adjusted at such low level as 2.1 ppm or less, increase in hexanal concentration was moderated. That is, by adjusting the dissolved oxygen concentration at such low level as 2.1 ppm or less, the spontaneous oxidation was controlled.

These results taken together with the results of previous examples demonstrate that spontaneous oxidation can be controlled by reducing dissolved oxygen concentration of raw milk, regardless of the way in which dissolved oxygen concentration is reduced and regardless of quality of raw milk.

Example 7

(Hexanal concentration, cooked flavor, and sulfides concentration for the case where dissolved oxygen concentration was reduced by a method of displacing oxygen with inert gas after a lapse of 24 hours from milking and then directly heated, and for the

case where dissolved oxygen concentration was reduced after a lapse of 24 hours from milking and retained for 24 hours in hermetic condition before heating)

Hexanal concentration, cooked flavor, and sulfides concentration were examined for the case where dissolved oxygen concentration was reduced after a lapse of 24 hours from milking and then directly heated, and for the case where dissolved oxygen concentration was reduced after a lapse of 24 hours from milking and retained for 24 hours in hermetic condition before heating.

For reducing dissolved oxygen concentration, a method of displacing oxygen with inert gas was used.

Over about 30 minutes after milking, the temperature of crude milk was cooled to 8°C. At this time the dissolved oxygen concentration of crude milk was 9.2 ppm (temperature: 8°C).

The crude milk for which the dissolved oxygen concentration was not adjusted was used as a reference sample (control) in the name of "unadjusted raw milk".

After a lapse of 24 hours from milking, unadjusted raw milk was aerated with nitrogen gas, and a total of four different samples of raw milk were prepared: the samples whose dissolved oxygen concentration was reduced to 2.0 and 5.0 ppm (temperature 7°C) and the samples which were retained for 24 hours in hermetic condition.

These samples of raw milk including samples of unadjusted raw milk after a lapse of 24 hours and 48 hours from milking were heated by autoclave (temperature 110°C, retention time 1 minute). These samples were named "unadjusted pasteurized milk", "pasteurized milk of low oxygen-2.0 ppm", "pasteurized milk of low oxygen-5.0 ppm", "unadjusted and retained pasteurized milk", "retained pasteurized milk of low oxygen-2.0 ppm" and "retained pasteurized milk of low oxygen-5.0 ppm".

In autoclave, raw milk was charged into a steel can (which is called "hermetic container") having excellent gas barrier property.

Figs. 12 to 14 show comparison results of dissolved oxygen concentration, hexanal concentration, cooked flavor, and sulfides concentration among unadjusted pasteurized milk, pasteurized milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, unadjusted and retained pasteurized milk, retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm.

Temporal change of dissolved oxygen concentration for unadjusted pasteurized milk, pasteurized milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, unadjusted and retained pasteurized milk, retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm was measured according to the method described in Example 1.

Fig. 12 shows temporal changes of hexanal concentration for unadjusted pasteurized milk, pasteurized milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, unadjusted and retained pasteurized milk, retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm.

Hexanal concentration was measured by the method described in Example 1.

Hexanal concentration of unadjusted pasteurized milk was 9 $\mu\text{g/L}$, and even after 24 hour-retention (unadjusted, retained pasteurized milk), the hexanal concentration was still as high as 9 $\mu\text{g/L}$.

On the other hand, hexanal concentration was 6 $\mu\text{g/L}$ for both of pasteurized milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, and even after 24 hour-retention (retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm), the hexanal concentration slightly increased but was still as low as 7 $\mu\text{g/L}$ for both cases.

When the dissolved oxygen concentration was adjusted at such low level as 5.0 ppm or less, hexanal concentration remained low.

In brief, when the dissolved oxygen concentration was adjusted at 5.0 ppm or less, spontaneous oxidation was controlled.

The lower the level at which the dissolved oxygen concentration of raw milk is adjusted, the greater the effect of controlling spontaneous oxidized flavor of pasteurized milk. In this Example, raw milk which is susceptible to spontaneous oxidation was used, however, even when the dissolved oxygen concentration of raw milk was adjusted at 5 ppm, the effect of controlling generation and increase of hexanal in pasteurized milk was achieved.

Fig. 13 shows evaluation of cooked flavor for unadjusted pasteurized milk, pasteurized milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, unadjusted and retained pasteurized milk, retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm.

Sensory evaluation of cooked flavor was carried out by 5-ranked evaluation by five special panelists as follows: 1 point (not sensed), 2 points (slightly sensed), 3 points (partly sensed), 4 points (sensed) and 5 points (strongly sensed), and average values were compared for each condition.

In unadjusted, and unadjusted and retained pasteurized milk, evaluation was 4.4 and 4.2, respectively, and almost all the special panelists sensed cooked flavor.

In low oxygen-2.0 ppm, low oxygen-5.0 ppm, low oxygen-2.0 ppm and retained, and low oxygen-5.0 ppm and retained pasteurized milk, the evaluation was 3.6, 3.4, 3.4 and 3.2, respectively, and all the special panelists partly sensed cooked flavor.

In any of pasteurized milk that was heated while dissolved oxygen concentration was reduced, cooked flavor was less sensed compared to unadjusted pasteurized milk.

In any stage, adjustment of dissolved oxygen concentration of raw milk at low level provides effect of controlling cooked flavor.

As is already mentioned, the earlier the timing at which dissolved oxygen concentration of raw milk is adjusted at low level, the greater the effect of controlling generation of hexanal concentration which is indicative of spontaneous oxidized flavor. Judging in comprehensive manner from these view points, controlling or managing dissolved oxygen concentration of raw milk in early stage after milking is effective for obtaining pasteurized milk having excellent quality and flavor.

In this Example, raw milk was placed in hermetic condition after reduction of dissolved oxygen concentration of raw milk, and then retained in a condition in which the dissolved oxygen concentration was low.

When raw milk is placed in open condition after reduction of dissolved oxygen concentration of raw milk, dissolved oxygen concentration increases and the effect of controlling cooked flavor of pasteurized milk is deteriorated to some extent. However, it would be expected that the effect of controlling cooked flavor is obtained by conducting pasteurization before dissolved oxygen exceeds 5 ppm.

At this time, the effect of controlling generation of hexanal concentration which is indicative of spontaneous oxidized flavor is achieved as well.

Fig. 14 shows area values of sulfides (area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS) in unadjusted pasteurized milk, pasteurized

milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, unadjusted and retained pasteurized milk, retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm.

Area value of sulfides was measured by solid-phase micro extraction method (SPME method) described below and a peak area value thereof was evaluated as concentration.

To be more specific, (1) sample (capacity: 10 mL) was collected in a vial container (capacity: 20 mL) and sealed. (2) The vial container is subjected to heating at 60°C for retention time of 40 minutes. (3) "Odor component" present in head space of the vial container is extracted by solid-phase microfiber (85 µm Stable Flex Carboxen/PDMS). (4) Analyze by GC-MS (column: CP-WAX) to determine area value of sulfides.

Now, area values of sulfides in low oxygen-2.0 ppm, low oxygen-5.0 ppm, low oxygen-2.0 ppm and retained, and low oxygen-5.0 ppm and retained pasteurized milk, are compared with area values of sulfides in unadjusted, and unadjusted and retained pasteurized milk.

As to area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS), the low oxygen-2.0 ppm, low oxygen-5.0 ppm, low oxygen-2.0 ppm and retained, and low oxygen-5.0 ppm and retained pasteurized milk showed tendency of being lower than those of unadjusted, and unadjusted and retained pasteurized milk.

Area values of sulfides in low oxygen-2.0 ppm, low oxygen-5.0 ppm, low oxygen-2.0 ppm and retained, and low oxygen-5.0 ppm and retained pasteurized milk were generally lower than area values of sulfides in unadjusted, and unadjusted and retained pasteurized milk.

In any stage, the effect of controlling generation and increase of sulfides was achieved by adjusting the dissolved oxygen concentration at 5.0 ppm or less.

As described above, the lower the dissolved oxygen concentration of raw milk is adjusted, the greater the effect of controlling generation and increase of hexanal concentration which is indicative of spontaneous oxidized flavor.

Based on the point that the lower the dissolved oxygen concentration of raw milk, the greater the effect of controlling deterioration in quality and flavor of raw milk which was in the environment in which off flavor is somewhat likely to occur, it can be

said that controlling or managing dissolved oxygen concentration of raw milk at low level is effective for obtaining pasteurized milk with good quality and flavor.

As described above, it seems that even if the raw milk is in open condition, comparable effect of controlling cooked flavor is obtained by carrying out pasteurization before the dissolved oxygen increases to 5.0 ppm or more.

In the present Example, area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS) were determined and considered. Other example of sulfides that are believed to be representative causative substance of cooked flavor is dimethyl sulfide (DMS). Considering the effect of controlling cooked flavor shown by experimental results illustrated in Fig. 13, and the tendency of area value of dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS) shown by experimental results illustrated in Fig. 14, it seems that the effect of controlling generation and increase of dimethyl sulfide (DMS) is also exerted by adjusting the dissolved oxygen concentration at 5.0 ppm or less.

Example 8

(Concentration of sulfides in raw milk subjected to reduction of dissolved oxygen concentration immediately after milking, after a lapse of 24 hours from milking, or after a lapse of 48 hours from milking by a method of displacing oxygen with inert gas prior to heating)

Sulfides concentration was examined for raw milk subjected to reduction of dissolved oxygen concentration immediately after milking, after a lapse of 24 hours from milking or after a lapse of 48 hours from milking prior to heating.

For reducing dissolved oxygen concentration, a method of displacing oxygen with inert gas was used.

Unadjusted raw milk was aerated with nitrogen gas immediately after milking, after a lapse of 24 hours from milking or after a lapse of 48 hours from milking, and for each case, the dissolved oxygen concentration was reduced to 0.8 ppm (temperature 7°C) to prepare three different samples of raw milk.

These samples of raw milk including samples of unadjusted raw milk after a lapse of 72 hours from milking were heated by autoclave (temperature 110°C, retention time 1 minute). These samples were named "unadjusted pasteurized milk",

"pasteurized milk of low oxygen-immediately after milking", "pasteurized milk of low oxygen-after a lapse of 24 hours from milking", and "pasteurized milk of low oxygen-after a lapse of 48 hours from milking".

In autoclave, raw milk was charged into a steel can (which is called "hermetic container") having excellent gas barrier property.

Fig. 15 shows comparison results of area values of sulfides among unadjusted pasteurized milk, pasteurized milk of low oxygen-immediately after milking, pasteurized milk of low oxygen-after a lapse of 24 hours from milking, and pasteurized milk of low oxygen-after a lapse of 48 hours from milking.

Fig. 15 shows area values of sulfides (area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS)) in unadjusted pasteurized milk, pasteurized milk of low oxygen-immediately after milking, pasteurized milk of low oxygen-after a lapse of 24 hours from milking, and pasteurized milk of low oxygen-after a lapse of 48 hours from milking.

Area values of sulfides were measured in the manner as described above.

Now, area values of sulfides in pasteurized milk of low oxygen-immediately after milking, pasteurized milk of low oxygen-after a lapse of 24 hours from milking, and pasteurized milk of low oxygen-after a lapse of 48 hours from milking are compared with area value of sulfides in unadjusted pasteurized milk.

As to area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS), pasteurized milk of low oxygen-immediately after milking, pasteurized milk of low oxygen-after a lapse of 24 hours from milking, and pasteurized milk of low oxygen-after a lapse of 48 hours from milking showed lower values compared to unadjusted pasteurized milk.

Area values of sulfides in pasteurized milk of low oxygen-immediately after milking, pasteurized milk of low oxygen-after a lapse of 24 hours from milking, and pasteurized milk of low oxygen-after a lapse of 48 hours from milking were generally lower than area values of sulfides in unadjusted pasteurized milk.

In any stage, the effect of controlling generation and increase of sulfides was achieved by adjusting the dissolved oxygen concentration at low level.

As described above, the earlier the timing at which the dissolved oxygen concentration of raw milk is adjusted at low level, the greater the effect of controlling

generation and increase of hexanal concentration which is indicative of spontaneous oxidized flavor.

Based on the viewpoint that the lower the dissolved oxygen concentration of raw milk, the greater the effect of controlling deterioration in quality and flavor of raw milk which was in the environment in which off flavor is somewhat likely to occur, it can be said that controlling or managing dissolved oxygen concentration of raw milk at low level in early timing after milking is effective for obtaining pasteurized milk with good quality and flavor.

As described above, it seems that even if the raw milk is in open condition, comparable effect of controlling cooked flavor is obtained by carrying out pasteurization before the dissolved oxygen increases to 5.0 ppm or more.

Example 9

(Concentration of sulfides in raw milk subjected to reduction of dissolved oxygen concentration after a lapse of 24 hours from milking by a method of degassing in vacuum atmosphere, prior to heating)

Sulfides concentration was examined for raw milk subjected to reduction of dissolved oxygen concentration after a lapse of 24 hours from milking, prior to heating.

In order to lower dissolved oxygen concentration, a method of degassing in vacuum atmosphere was used.

The method of degassing in vacuum atmosphere shown in Example 5 was applied to unadjusted raw milk after a lapse of 24 hours from milking, and the dissolved oxygen concentration was reduced to 2.1 ppm (temperature 7°C) from 11.2 ppm (temperature 8°C).

These samples of raw milk were heated by autoclave (temperature 10°C, retention time 1 minute) (these samples are named "unadjusted pasteurized milk" and "low oxygen (degassed)-2.1 ppm pasteurized milk", respectively.)

In autoclave, raw milk was charged into a steel can (which is called "hermetic container") having excellent gas barrier property.

Fig. 16 shows comparison results of area values of sulfides between unadjusted pasteurized milk and low oxygen (degassed)-2.1 ppm pasteurized milk.

Fig. 16 shows area values of sulfides (area values of dimethyl disulfide

(DMDS) and dimethyl trisulfide (DMTS)) in unadjusted pasteurized milk and low oxygen (degassed)-2.1 ppm pasteurized milk.

Area value of sulfides was measured in the manner as described above.

Now, area values of sulfides in low oxygen (degassed)-2.1 ppm pasteurized milk are compared with area value of sulfides in unadjusted pasteurized milk.

As to area values of dimethyl disulfide (DMDS), low oxygen (degassed)-2.1 ppm pasteurized milk showed lower value compared to unadjusted pasteurized milk.

As to area values of dimethyl trisulfide (DMTS), low oxygen (degassed)-2.1 ppm pasteurized milk showed comparable value with unadjusted pasteurized milk.

Area value of sulfides in low oxygen (degassed)-2.1 ppm pasteurized milk was generally lower than area values of sulfides in unadjusted pasteurized milk.

In comprehensive consideration of the results of the above Examples, it can be concluded that generation of sulfides can be controlled by reducing dissolved oxygen concentration of raw milk regardless of the method of reducing dissolved oxygen concentration such as the method of degassing in vacuum atmosphere and the method of displacing oxygen with inert gas.

It seems that even if the raw milk is in open condition, comparable effect of controlling cooked flavor is obtained by carrying out pasteurization before the dissolved oxygen increases to 5.0 ppm or more.

Brief Description of the Drawings

[Fig. 1]

A graph showing temporal changes of dissolved oxygen concentration for the case where dissolved oxygen concentration of raw milk is not adjusted, and for the cases where dissolved oxygen concentration is reduced immediately after milking and retained in an open container and a hermetic container.

[Fig. 2]

A graph showing temporal changes of beany flavor for the case where dissolved oxygen concentration of raw milk is not adjusted, and for the cases where dissolved oxygen concentration is reduced immediately after milking and retained in an open container and a hermetic container.

[Fig. 3]

A graph showing temporal changes of hexanal concentration for the case where dissolved oxygen concentration of raw milk is not adjusted, and for the cases where dissolved oxygen concentration is reduced immediately after milking and retained in an open container and a hermetic container.

[Fig. 4]

A graph showing temporal changes of dissolved oxygen concentration for the case where dissolved oxygen concentration of raw milk is not adjusted, for the case where dissolved oxygen concentration is reduced immediately after milking, for the case where dissolved oxygen concentration is reduced after a lapse of 24 hours from milking, and for the case where dissolved oxygen concentration is reduced after a lapse of 48 hours from milking.

[Fig. 5]

A graph showing temporal changes of hexanal concentration for the case where dissolved oxygen concentration of raw milk is not adjusted, for the case where dissolved oxygen concentration is reduced immediately after milking, for the case where dissolved oxygen concentration is reduced after a lapse of 24 hours from milking, and for the case where dissolved oxygen concentration is reduced after a lapse of 48 hours from milking.

[Fig. 6]

A graph showing temporal changes of dissolved oxygen concentration for the case where dissolved oxygen concentration of raw milk which is susceptible to spontaneous oxidation is not adjusted, and for the case where dissolved oxygen concentration is reduced to 0.8 ppm immediately after milking.

[Fig. 7]

A graph showing temporal changes of hexanal concentration for the case where dissolved oxygen concentration of raw milk which is susceptible to spontaneous oxidation is not adjusted, and for the case where dissolved oxygen concentration is reduced to 0.8 ppm immediately after milking.

[Fig. 8]

A graph showing temporal changes of dissolved oxygen concentration for the case where dissolved oxygen concentration of raw milk which is insusceptible to spontaneous oxidation is not adjusted, for the case where dissolved oxygen

concentration is reduced to 2.0 ppm after a lapse of 24 hours from milking, and for the case where dissolved oxygen concentration is reduced to 5.0 ppm after a lapse of 24 hours from milking.

[Fig. 9]

A graph showing temporal changes of hexanal concentration for the case where dissolved oxygen concentration of raw milk which is insusceptible to spontaneous oxidation is not adjusted, for the case where dissolved oxygen concentration is reduced to 2.0 ppm after a lapse of 24 hours from milking, and for the case where dissolved oxygen concentration is reduced to 5.0 ppm after a lapse of 24 hours from milking.

[Fig. 10]

A graph showing temporal changes of hexanal concentration for the case where dissolved oxygen concentration of raw milk which is susceptible to spontaneous oxidation is not adjusted, and for the case where dissolved oxygen concentration is reduced to 2.1 ppm after a lapse of 24 hours from milking.

[Fig. 11]

A graph showing temporal changes of hexanal concentration for the case where dissolved oxygen concentration of raw milk which is insusceptible to spontaneous oxidation is not adjusted, and for the case where dissolved oxygen concentration is reduced to 2.1 ppm after a lapse of 24 hours from milking.

[Fig. 12]

A graph showing hexanal concentration for the case where heating was conducted without adjustment of dissolved oxygen concentration of raw milk, for the cases where dissolved oxygen concentration was reduced to 2.1 ppm and 5.0 ppm after a lapse of 24 hours from milking, and then heating was conducted, and for the cases where dissolved oxygen concentration was reduced to 2.1 ppm and 5.0 ppm after a lapse of 24 hours from milking, followed by 24 hours retention in hermetic condition before conducting heating.

[Fig. 13]

A graph showing cooked flavor for the case where heating was conducted without adjustment of dissolved oxygen concentration of raw milk, for the cases where dissolved oxygen concentration was reduced to 2.1 ppm and 5.0 ppm after a lapse of 24 hours from milking, and then heating was conducted, and for the cases where dissolved

oxygen concentration was reduced to 2.1 ppm and 5.0 ppm after a lapse of 24 hours from milking, followed by 24 hours retention in hermetic condition before conducting heating.

[Fig. 14]

A graph showing area values of sulfides (area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS)) in pasteurized milk which is heated without conducting adjustment of dissolved oxygen concentration of raw milk, pasteurized milk of low oxygen-2.0 ppm, pasteurized milk of low oxygen-5.0 ppm, unadjusted and retained pasteurized milk, retained pasteurized milk of low oxygen-2.0 ppm and retained pasteurized milk of low oxygen-5.0 ppm.

[Fig. 15]

A graph showing area values of sulfides (area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS)) in pasteurized milk which is heated without conducting adjustment of dissolved oxygen concentration of raw milk, pasteurized milk of low oxygen-immediately after milking, pasteurized milk of low oxygen-after a lapse of 24 hours from milking, and pasteurized milk of low oxygen-after a lapse of 48 hours from milking.

[Fig. 16]

A graph showing area values of sulfides (area values of dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS)) in pasteurized milk which is heated without conducting adjustment of dissolved oxygen concentration of raw milk, and low oxygen (degassed)-2.1 ppm pasteurized milk.

CLAIMS

1. A method of controlling off flavor in raw milk and pasteurized milk, comprising conducting a treatment of reducing dissolved oxygen concentration in a course between milking to pasteurization in processing of bovine milk.

2. The method of controlling off flavor in raw milk and pasteurized milk according to claim 1, wherein the treatment of reducing dissolved oxygen concentration is conducted within 72 hours after milking.

3. The method of controlling off flavor in raw milk and pasteurized milk according to claim 1 or 2, wherein the dissolved oxygen concentration is kept low after conduction of treatment of reducing dissolved oxygen concentration until pasteurization.

4. The method of controlling off flavor in raw milk and pasteurized milk according to any one of claims 1 to 3, wherein control of off flavor is achieved by conducting at least one of the following controls:

- (1) control of spontaneous oxidized flavor in raw milk;
- (2) control of generation and/or increase of hexanal;
- (3) control of cooked flavor; and
- (4) control of generation and/or increase of sulfides.

5. The method of controlling off flavor in raw milk and pasteurized milk according to claim 4, wherein the spontaneous oxidized flavor is beany flavor.

6. The method of controlling off flavor in raw milk and pasteurized milk according to claim 4, wherein the sulfides is at least one selected from the group consisting of dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS).

7. Pasteurized milk processed by using the method of controlling off flavor in raw milk and pasteurized milk according to any one of claims 1 to 6.