I. Characterization and Concepts

Fish marinades are characterized by typical odors and flavors; these arise from the treatment of fish or parts of fish with vinegar and salt. This treatment simultaneously brings about a refinement, i.e., conversion of the raw product into food, and a certain preservation. The resulting odor and flavor effects are accentuated by the addition of various spices and covering liquids. The preserving principle is the combination of vinegar and salt (in cooked and fried marinades there is also brief heat treatment). Since it is not feasible, for reasons of taste, to increase the amount of additives in order to suppress possible spoilage, marinades can be kept only for a certain period of time; they are therefore classed among the semi-conserves. Additional preservation by heat sterilization is in general not possible since their characteristic nature would then be lost. Only fried marinades can be treated in this way, to some extent.
On the basis of preparative procedures, cold, fried, and cooked marinades may be distinguished. In cold marinades, or marinades proper, the fish are treated in a so-called finishing bath\(^1\) with a relatively high vinegar and salt content in which they are kept for about a week. In contrast, fried marinades are processed by heating in oil or fat, and cooked marinades are prepared by bleaching\(^2\) in vinegar-salt solutions. The only property in common with the cold marinades, then, is their decidedly acid character, caused by the acidic brines or sauces in fried marinades and by the acidic jelling in cooked marinades.

In the guiding principles for the evaluation of fish products, elaborated by the Federal Association of German Fish Industries (1957), therefore, the term “marinades” has been dropped for the first time with reference to the latter two groups of products, and the terms “fried fish products” and “cooked fish products,” respectively, have been substituted for it. The pH value of 4.8 serves to delineate them from sterilized products likewise prepared with acidic brines or sauces, but which are less acid.

\section*{II. Individual Products}

Since marinades are products made primarily in Europe and in particular in Germany, the use may be permitted in each instance of the terminology developed along the guiding principles indicated above. Accordingly, marinades (called “cold marinades” in the previously used terminology) are fish products consisting of fresh, frozen, or salted fish or portions of fish processed by treatment with edible acids and salt with the use of adjuvants for seasoning and bleaching and put up in brines, sauces, creams, mayonnaise, remoulade, or oil.

\subsection*{A. Cold Marinades}

In Europe, only herring and sprat are really suitable for the preparation of cold marinades. Both yield a delicate product of fine taste if handled properly. The terminology for the various cold marinades is based essentially on the type of preparation; the presence or absence of the dorsal fishbone is an important criterion.

The chief product is pickled flesh of herring obtained after the head, viscera, and central bone have been removed in such a way that the two fillet lobes are still connected in the back. This is a semi-prepared product, which is sold as such (previously by the name of “saure Lappen” meaning “sour lobes”). “Bismarck herring,” “marinated herring fillets,”

\begin{footnotesize}
\begin{enumerate}
\item The term “finishing bath” may be considered synonymous with “pickling bath,” “marinating bath,” or “garbad,” as may appear in other literature.
\item The term “bleaching bath” has the same meaning as the term “blanching bath” sometimes used in other literature.
\end{enumerate}
\end{footnotesize}
5. MARINADES

and "collared herring" are derived from it. Bismarck herring are put up in clear vinegar brine with black pepper, mustard seeds, and slices of onion. If the two halves of the fillet are separated the product is called marinated herring fillets, or marinated herring fillet pieces when the fillets are further subdivided transversely. The clear cover brine is then usually replaced by a covering sauce, mayonnaise, or remoulade. Collared herring are prepared from rolled, pickled herring flesh, with seasoning consisting of pickled cucumber and onions placed in the center of the roll. The tail section is previously removed. Fork-sized collared herring are bite-sized small collared herring with or without skin.

The prototype of marinades with a central bone is the so-called "delikatess herring," which is eviscerated and headless. Pickled or marinated herring is prepared principally from salted herring (but also from fresh herring) with or without heads. It originally gave rise to the cold marinades. Because of its hearty taste, it is still prepared by many housewives or offered by restaurants with the note "prepared home-style." Preserved herring also belong to this group of marinades, manufactured from salted herring. They differ in general because the central fishbone has been removed.

The last group to be considered is that of the "crown sardines" or "Russian sardines" which are not derived from sardines, as the name might suggest, but rather from small herring in which the viscera and the head have been removed. Sprat may also be used to prepare a similar product.

For cold marinades, a vinegar-salt cover brine is employed containing whole spices and slices of onions, which at the same time serves to give a garnishing effect. To soften the acid taste, vinegar treated with a saccharin may be used since there is danger of fermentation if sugar is added. Besides such pickling solutions, special sauces and mayonnaise are employed. Marinades, prepared from selected raw products and packed with particularly tasty pickling solutions, sauces, etc., or other valuable additives, are considered luxury marinades. If necessary the skin, especially the dark ventral skin, is first removed. These products may not, however, be prepared with the use of bleaching agents or saccharin.

B. COOKED MARINADES

Cooked marinades are made with fresh or frozen fish or portions of fish, processed with salt and edible acids and then heat treated. Seasonings or jelling substances may be added. Special covering sauces are also employed.

Since all the products of this type, with the single exception of sea-
soned eel, are packed in a jelly, they are termed jellied products. In addition to herring, the following are made into jellied products: eel, thornfish, mackerel, river lamprey, smelt, and other marine fish as well as shrimps and mussels.

To make herring in jelly, use is commonly made of pieces (chunks) of eviscerated herring, divided transversely to the central bone; nowadays the central bone is usually removed. To make collared herring in jelly, fillets are rolled around small pieces of cucumber with spices. If smoked bacon fat is used as a further additive, the term “collared herring with bacon” is employed. Eel in jelly and thornfish (spiny dogfish) in jelly correspond to herring in jelly in type of preparation. Fish jelly made from (diced) salt-water fish flesh (especially from gadids) also belongs to this group. A transition to the fried marinades is provided by fried herring of various types, such as fried fillets and fried collared herring in jelly. Finally, buckling fillets and smoked collared herring are also made into jellied products.

C. Fried Marinades

Fried marinades are fresh or frozen fish or parts of fish which are fried, baked, or broiled in oil or fat with or without breading and covered with vinegar solutions or sauces.

In contrast to the cold marinades, the raw products for these items include many types of fish in addition to herring, for example, eel, river lamprey, haddock and other gadids, smelt, and several types of flatfish. Most fried fish are prepared and eviscerated, generally with the head removed but usually with the backbone remaining. Frying with the head and viscera is no longer in accordance with practice and should be permitted only with river lamprey. Another common procedure is the frying of herring chunks and fish cutlets, meaning fish cut transversely to the central bone; the corresponding portion of the backbone remains in the flesh. A specialty consists of fried collared herring prepared from rolled herring fillets sprinkled with spice grains. Spices are also in the center, similar to what was described for collared herring (Section II, A).

Fried fish products are in general packed in a spiced vinegar pickle (malt vinegar); fried herring fillets, on the other hand, may be put in a piquant covering sauce, e.g., the skumbria sauce of the Baltic states.

III. Manufacturing Procedures

A. Cold Marinades

1. Pretreatment

As soon as the fish arrive in the plant, they must be freed of dirt and scales as rapidly as possible. This is most easily done in so-called drum
washers which guarantee careful treatment. With particularly soft prod-
ucts, first a bath of 8–10% salt for about 1 hour to achieve hardening is
recommended. The drum washers also provide the possibility for a con-
tinuous process. The products are then decapitated, eviscerated, and de-
boned, according to type of product, in modern deboning machines, a
procedure also employed commonly in the production of sterile pre-
serves. To conduct the washing after cutting would be less satisfactory
from a sanitary point of view. The cutting involves spreading of filth
and bacteria in the flesh.

The fish or portions of fish are subsequently placed in a second cleans-
ing bath, the so-called exsanguination bath in which the blood is removed
as completely as possible from the flesh. This is facilitated by the addi-
tion of 3–5% salt, but fish should not be kept in this solution longer than
a half-hour, since there is danger of reverse diffusion.

For transport from catching grounds to processing plant, herring are
usually sprinkled with salt. In this procedure an uneven distribution of
salt cannot be avoided. Such inequities may be corrected in the blood-
removing bath. In earlier days it was customary to carry out a bleach
by addition of hydrogen peroxide up to 50 g. of 30% hydrogen peroxide
solution to 100 liters of the blood-removing bath. Regardless of the legal
situation, this type of bleaching is costly in terms of aroma losses and
enhances rancidity. This method has therefore been discarded, particu-
larly since the dark ventral skin is also removed in modern deboning
machines. A small degree of bleaching can be achieved by addition of
0.5% acetic acid to the bath. The fish can in this case be allowed to drip
dry on the surface in order to avoid subsequent dilution of the vinegar-salt
bath through adhering water. Following this pretreatment, the product
is introduced into the softening (finishing) bath.

If salted herring are to be used, they must be soaked prior to cutting,
preferably by holding under running water for 24 hours. In products
which are not to be deboned, a cut must be made with a knife along
the central bone to allow better penetration of the finishing bath liquid
into the dark flesh stripes of the salt herring. After cutting, the fish are
soaked for an additional 4 hours. Complete desalting is to be avoided.
Salted herring in which oil decomposition has taken place are not
suitable for the preparation of marinades.

2. Finishing Bath

The proper composition of the finishing bath, the ratio of fish to
liquid, and the exact manner of treating the product are of decisive im-
portance to a successful final quality. Acetic acid is naturally the most
important ingredient of the pickling solution. But without an adequate
portion of salt the softening process would proceed too far, and in
particular the skin would become detached from the flesh. While acetic acid softens the fish flesh, it is hardened by the salt. On the basis of empirical experience, salt should be in an amount 1-7% higher than that of acetic acid, depending on the strength of the finishing bath. The ratio of fish to pickle liquid must be balanced through so adjusting the acetic acid concentration that the finishing bath at the end of the manufacturing process has an acetic acid concentration of at least 2.5%. Since the keeping quality is reduced with increasing temperature, this concentration must be raised during the warmer seasons of the year. It depends in addition on the water content of the raw products (see below). The more pickle liquid used, the easier it becomes to stir the contents but the total amount of liquid and vinegar required is increased.

The most common vessels for pickling until recently were large open wooden vats or basins protected by acid-fast tiles. These vessels were set up in basements or cool rooms. The ratio of fish to pickling liquid was 1:1 to 3:2, depending on the available vessel volume. Further increase in the amount of fish per volume is not possible because the vinegar-salt concentration then becomes so high that the specific gravity of the finishing bath rises above that of the fish. As a consequence, the fish would then move to the surface and protrude from the liquid. This would lead to defective products. In the last few years, therefore, finishing in closed vats (mostly in Norwegian barrels holding 114 liters) has come to the fore. In this way the vats can be stacked in several layers and the products transported in the vats. In this case 80 kg. herring are generally placed in 35 kg. finishing bath 2.3:1 with 7% acetic acid and 14% salt. For pickling in open vats a 3:2 ratio of fish to liquid with 6% acetic acid and 10% salt is considered best.

The content of acetic acid required in the finishing bath can be calculated according to the formula \( E = 0.125 \times [20 + 0.3(H_2O + \text{protein})] \) for open vat refining at 3:2, or \( E = 0.083 \times [30 + 0.7(H_2O + \text{protein})] \) for closed vats if the marinating solution at the end of treatment is to contain 2.5% acetic acid. Corresponding formulas can be set up for every ratio between fish and liquid as well as for other percentages of acetic acid in the final finishing bath. Under otherwise identical conditions, 3.5 kg. acetic acid is required for 100 kg. herring with a water content of 60% in open vats, and 2.9 kg. acetic acids in closed vats, still assuming a final acid concentration of 2.5%. In general, the liquid is not weighed out but measured by volume since this is simpler. It is true that with a higher salt content the specific gravity of the finishing bath becomes greater; in closed vats the acetic acid content in the final liquid is raised by 0.2% due to this factor. But this error can be neglected, the more so since it provides a safety factor.
In order to be on the safe side, when the fish have a high water content of 72%, protein 16%, and fat 10% (the lowest figures acceptable for the preparation of cold marinades), calculation of the amount of acetic acid in the original pickling solution is obtained simply by multiplying by the ratio factor, as for example by the fish:liquid ratio of 3:2, resulting in 2.32 in open vats and 3.05 in closed vats.

For marinades of salted herring, a finishing bath with 5% acetic acid and 3% salt is recommended at a fish:liquid ratio of 2:1. The addition of hydrogen peroxide as a bleaching agent up to 60 ml. 30% solution per 100 liters of the pickling solution is desirable. However, the legal provision of each country must be borne in mind.

The essential factor for preservation is the acetic acid. Therefore all portions of the fish must be brought in contact with the acid, uniformly and quickly. To achieve this goal, it is advisable to place the fish in the pickling bath, to “slap them in,” one by one; fillets which hang together are folded back. In closed vats, this precaution is quite essential. It is further necessary that the entire amount of the marinating solutions be added not all at once but in portions, layer after layer, in the way commonly employed in the salting of herring. Otherwise the marinating liquid may become too diluted by water diffusing from the fish tissue. This precautionary measure may seem time-consuming and expensive, particularly since it has been carried out manually until quite recently. Nevertheless it is crucial to satisfactory marinating. According to a recent German patent, this procedure can be mechanized. The addition of marinating liquid can also be simplified by the use of dosimeters (Bruhn, 1956). Loss in weight of the fish at the end of the marinating amounts to about 15%.

During the pickling period which is concluded in 3–7 days, depending on temperature—optimally at 10–12°C.—it is necessary to ensure by repeated stirring, particularly at the start, that the various portions of fish do not stick together, as this prevents rapid penetration of the acetic acid into the center of the product. In open vats stirring is done with broad wooden poles; in closed vats, mixing is achieved either by rolling when taking the barrels to storage or by rotating them on special rotor machines. Upon completion of the finishing treatment, the product is either placed in coolers or packed immediately, as required.

3. Packing

For packing, the fish are removed from the barrels, rinsed briefly, and poured onto sorting tables. A successfully completed finishing process can be recognized by the condition of the fish flesh. It may no longer be glassy or shiny in the innermost portions of the flesh; red spots indi-
cate defective finishing. Such products do not keep and must be discarded. It is further advisable to look for damaged products; one or another fish may have to be cleaned again if necessary.

In addition to wooden barrels, the packaging materials may include tin cans of various sizes, depending on whether the product is intended for retailing to the ultimate consumer. The most common sizes are cans with a content of 6.6 or 3 liters (diameter 230 mm., 170 mm. or 83 mm. high). Smaller cans are more suitable for retailing, e.g., diameter of 99 mm. and height of 33 mm. holding 210 ml., or 135 mm. and height of 33 mm. holding 425 ml. (for herring rolls as well as fillet products in sauces and mayonnaise or related products). There are various other intermediate sizes, including rectangular and oval cans. Cans should be provided on the inside with a good lacquer; otherwise there is great risk of chemical damage. Glass and plastic containers have been used recently with success.

The ratio of fish to cover brine or covering sauce is about 2:1; there may be a deviation from this ratio under certain conditions, if a fixed number of fish are to be in the can. The cover brine contains 1–2% acetic acid and 2–4% salt, the lower values applying to cold and the higher ones to warm seasons. A particularly aromatic brine is provided by taking the finishing bath liquid, suitably diluted. Bacteria are largely removed by ultra filtration.

The acid taste of the marinades may be softened by spices or by vinegar to which saccharin has been added. The amount of such a compound should correspond to the sweetening power of 2.5% cane sugar. Slices of onion, carrot, or celery or pieces of cauliflower may serve as garnish. These adjuncts must first be pickled; the vegetables must in addition be blanched. If spices such as pepper, mustard, pimento, etc. are added merely for taste purposes, spice extracts are recommended since they are in general germ-free. Special investigations are in progress at the present time to reduce the acid taste by other procedures and to strengthen the characteristic aroma of the product.

Whereas in the case of marinated products the cans are simply filled to the rim with the covering liquid, special filling machines are used for sauce products. The cans are closed with regular sealing machines. Since the covering brine is liquid, the cans must not rotate during sealing. This holds for all marinades.

4. Recovery of Used Brine

During the finishing or softening process the fish lose about 15% of their weight by giving off water to the finishing bath, so that this represents almost one half the total quantity even when the initial ratio of
fish to finishing bath is 3:2. If the bath had an initial content of 6% acetic acid and a final value of 2.5%, then over half the acetic acid is lost when disposing of the remaining pickling bath. A prerequisite for using such liquid again is good quality of appearance, odor, and taste.

Such used pickle brine may be employed for making up new cover brine by carrying out a suitable dilution to half or one-third strength; under proper circumstances it may even have a very fine taste. Appropriate filtration can remove any turbidity which may have appeared or undesirable microorganisms.

Even under ideal conditions one may use only half the available spent baths in this way. Certain tax regulations in Germany hinder re-use of these old pickle brines. Tax-favored salt may be used in making up new baths, but not for cover brines.

A further possibility consists in the re-use of the finishing bath after renewal through adding acid up to its original level. The reconstituted finishing bath must be filtered to remove turbidity and to eliminate microorganisms. For this purpose, the finishing bath which still contains appreciable amounts of proteinaceous components in colloidal form is treated with suitable precipitants such as hydrogen peroxide (Lücke et al., 1938) or with colloidal silicon. After allowing the mixture to settle, preliminary purification can be carried out by centrifuging and final purification with presses equipped with filters which retain microorganisms.

Since the finishing baths are often colored a very intense yellow, activated carbon or similar materials may have to be added to the material prior to filtering. This type of recovery necessitates certain technical equipment and a special command of filtration techniques, which are frequently not available in small fish-processing plants and are not economic on a minor scale. This regeneration process must, moreover, be checked continuously as to microbial counts.

It is important that the renewal with acetic acid be carried out prior to filtration, since otherwise further turbidity may be produced by addition of the acid. This seems to be the only way in which further development of microorganisms can be averted. This re-use should, of course, only take place once, since the storage of finishing baths for longer periods requires too much space and is too risky from the microbial point of view.

Since the used finishing baths exhibit a higher pH value (about 4.4) than a freshly made solution (about 2.7), it is often assumed that the acetic acid contained in it is no longer active. These fears are not justified because the effectiveness of the finishing process does depend on the titratable acidity. The pH value simply indicates that buffering substances have entered the finishing bath. Since these buffer substances, however,
may be amino acids which aid in the development of gas-forming microorganisms, the finishing bath cannot be re-used too many times. Otherwise, too many of these amino acids accumulate and the threshold value for gas formation is rapidly exceeded. As long as more precise investigations on this point are not available, it may be advisable not to try a second re-use of the finishing bath.

B. COOKED MARINADES

1. Pretreatment

Only fish of highest quality are suitable for the preparation of cooked marinades. Raw products which tend to become rancid easily do not lend themselves too well to the manufacture of good final products. Jellied products should not be strongly spiced. Rather, the specific aroma of the corresponding raw product should be brought out as effectively as possible by the jellied brine. The most meticulous preliminary cleaning to remove dirt and scales is an important prerequisite. It is carried out much in the same manner as described above for cold marinades.

Appropriate machines are used for beheading and evisceration of the herring. By contrast, the backbone is not removed; rather, the herring is cut into chunks. These pieces must be of somewhat larger size than the intended size of the final portions, since they shrink considerably by treatment in the bleaching bath. Other fish may have to be eviscerated by hand. Thorough final cleaning is urgently required in all instances.

The blood is removed by placing the fish for about 30 minutes in a bath with 10% salt; this treatment constitutes at the same time a kind of preliminary salting.

2. Bleaching

The products are spread out on flat sieves (about 5 kg. per sieve of dimensions 640 × 55 mm.) and several sieves one above the other are placed in the bleaching bath. At 85°C. the flesh is usually ready in 10-15 minutes. Larger fish or pieces of fish may require longer exposure. The bleaching bath usually contains 1–2% acetic acid, on rare occasions 4% and 6–8% salt, depending on the preliminary salting. The bleaching bath must be renewed from time to time. Instead of bleaching in a vinegar-salt solution, the fish may be refined in a steam cabinet.

As soon as the product has left the bleaching bath, it is rinsed free of adhering fat and protein foam and cooled with cold water.

3. Packing

After cooling and air-drying it is packed. For retail sale the jellied products are packed chiefly in four-sided cans (240 × 230 × 40 mm. for
3 × 4 portions, or 240 × 230 × 71 mm. for 24 portions in two layers). If the product is to be sold locally, making lengthy transportation or storage superfluous, glass or porcelain vessels are used. Each unit weighs about 140 g. and contains 70 g. fish, since jellied products normally contain fish and jelly in about equal proportions. In unpacked products, the jelly portion must be larger (1 part fish and 3 parts jelly); otherwise there is danger from premature drying of the jellied fish that the pieces may protrude, leading to possible mold growth on the exposed surface. If the product is to be sold in closed containers to the ultimate consumer, small round cans (99 × 33 mm., 135 × 33 mm., and even 160 × 48 mm.) may be used. Plastic containers and paraffin-coated paper cup packs may be employed in this instance. Tin cans should be lacquered.

The concentration of acetic acid in the jellied brine is of decisive importance, since it determines the pH value of the entire product and thus its keeping qualities. At the usual ratio of 1:1 between fish and marinating medium, the latter must contain at least 1.9-2% acetic acid. In summer, it is preferable to raise the concentration still further. The salt content should be correspondingly about 3%; in attaining this level, the presalting of the raw product must be taken into account. The required amount of gelatin depends on its quality. The storage temperature of the cooked marinades exerts some influence. In general a 4-5% concentration of gelatin is appropriate. Since gelatin is very heat-sensitive, care must be taken in the preparation of the jellied brine that the temperature does not rise above 70°C. Spices and saccharin can be added to the jellied pickling brine. In the filling, the brine is cooled down to 40°C.

To keep portions of fish from lying directly on the bottom, a 5-mm. layer of jelly is first poured into the containers and allowed to solidify. Then the fish are packed onto the jelly in such a way that the individual pieces do not touch each other. In jellied herring, the backbone is removed by carefully separating the halves of the fish. In cans containing several layers, the jelly must be allowed to solidify each time before the next layer is packed. In order to separate the individual layers, a piece of perforated parchment paper is inserted. Garnishings such as slices of carrot and onion or cooked eggs, etc. are placed on the penultimate layer. Before closing the can, a last layer of jelly is poured on top and covered with a piece of parchment paper to prevent the jelly from adhering to the cover. It is important that this brine, added last, also called the “mirror” layer, fill the can completely. Even before solidification, the can is sealed. The jelly is chilled by special devices such as tunnels, etc. Before the product is shipped, it should be stored for 24 hours in a cooler for reasons to be discussed below.
C. Fried Marinades

1. Pretreatment

Cleaning, cutting, removal of blood, and presalting are carried out in the same way as described for cold and cooked marinades. After the fish or fish pieces have been allowed to drain well, they are treated twice in a breading mixture composed of equal parts of rye and wheat flour. After the first breading, the fish must be left to lie for at least an hour to give the meal time for soaking. The breaded fish are then moistened once more and can absorb a second breading. Excess meal must be tapped off gently to avoid the appearance of lumps.

2. Frying

Highly varied devices can be used for frying. The original arrangement was an open pan heated directly by coal. The trend toward standardization led to (1) the immersion pan in which the fish are fried, (2) the turnstile pan, and (3) frying devices with conveyor belts arranged in a manner similar to that in the bleaching procedure in which time of passage and heating can be controlled automatically. The time for removal of excess adhering frying oil during transport from the pan is also arranged automatically. For the immersion pans, the breaded fish are placed on metal sieves. Since fish baked in the frying pan according to home-style offer taste advantages over oil-fried fish, mechanization of the former process has also been accomplished. The most recently developed device is so arranged that the fish are just barely covered with frying oil. The technical advantages consist in better heat utilization, smaller oil consumption, and easier water evaporation. The process of packing the fish onto sieves is sometimes eliminated. The conveyor belt permits the attachment of a second belt for the chilling of the fried fish in a tunnel. Then the fish may be taken from the belt and packed directly into the cans.

The frying oil consists of a mixture of oil and solid fat to obtain a pliable film of fat all around the fish. In warmer seasons, one may increase the percentage of solid fat, in colder seasons that of oil.

Frying temperatures in oil should be between 160°C. and 180°C., the latter being optimal. Frying time depends on the temperature of the frying oil, the thickness of the fish, and their water content. Duration of the frying process may accordingly be between 5 and 12 minutes. In immersion pans, the termination of the frying process is indicated by the rise of the fried fish to the surface, since their specific weight is altered by loss of water and absorption of fat.
5. MARINADES

3. Packing

After the fried fish is well cooled, they are packed into cans of various sizes depending on whether they are to be sold in bulk or retail. The ratio of fish to covering liquid is about 2:1, depending on the ability of the fried fish to take up the fluid. In frying, the fish lose about 20% of their water. Much of this is later taken up again from the surrounding liquid. Since this reabsorption does not take place instantaneously, the filled cans are allowed to stand open for several hours and then filled to the brim and sealed. The brine has an acetic acid content of 2.0–3.5% and a salt content of 3–5%, depending on the season and water content of the product. The use of malt vinegar, or vinegar containing herbs or spices, is recommended. A softening of the acid taste by adding saccharin can also be carried out at this stage. Spices in solid form may be pimento, mustard seeds, cloves, or laurel leaves. If the product is to be sold not only by weight but by the piece, the fish must be sorted according to size.

IV. Keeping Properties

In view of the manner of their preparation, marinades are stable only for a limited period of time. For cold marinades, the only available preservatives are acetic acid and salt. For cooked and fried marinades, there is the additional heat treatment step which induces a maximum temperature in the flesh of just under 100°C. This heat treatment is not sufficient to kill all microorganisms. There is, moreover, the possibility of subsequent contamination up to the time when the cans are sealed. The keeping qualities depend largely on storage temperatures, but probably also on the type of bacteria and their temperature requirements. If the finished products are kept at 27–30°C, spoilage must be assumed to occur after about 20 days, even if they were adequately prepared. Spoilage is indicated principally by gas formation which leads to swelling of the cans; with fried marinades it may also involve the appearance of slime, and with jellied products there may be liquefaction. If the cans are not sealed properly or are filled inadequately, jellied products may exhibit mold growth.

There are different types of spoilage, which may be classified according to their causes into physical, chemical, and biological types.

A. Physical Spoilage

Physical spoilage is caused by purely mechanical factors. Cold damage occurs when the products are stored at temperatures below 0°C.
Water expands in the freezing (in cooked marinades the jelly is torn apart by the formation of ice crystals, mayonnaise separates out). Heat damage occurs if the cans are filled in too cold an atmosphere, are too full, and are then stored in a warm environment. With fried marinades, the cans may swell if sealed too early before the swelling of the flesh is completed. Packing damage occurs if the can swells at the time of sealing because it is too full. Finally, compression damage may come about if cans are crushed or deformed in closing or shipping. With very few exceptions the contents of the can are barely altered by physical spoilage. The swelling of the cans is also more or less negligible; it scarcely goes beyond the stage of flipping.

B. CHEMICAL SPOILAGE

Chemical spoilage is caused by attack of strongly acid products on the metal of the cans, tinned or poorly lacquered. Hydrogen gas is formed. In addition to the swelling the contents of the can may have a metallic taste, caused by metal dissolved in the products, and thus become unpalatable.

C. BIOLOGICAL SPOILAGE

Of greatest significance is the biological spoilage, which may exhibit all gradations from simple flipping to the most pronounced swelling and even bursting of the cans. There are two subcategories: (1) protein spoilage, derived more or less from the microbial degradation of protein originating in the fish itself, and (2) carbohydrate spoilage, caused by fermentation of added sugars or other sugar-containing additives. A special case of biological spoilage is caused by catalase. If too much hydrogen peroxide is added in connection with the use of raw vegetables, e.g., onions, oxygen is formed by the catalase enzyme.

To avoid these types of spoilage, it is of course necessary to know their precise causes. It is easy to distinguish them by means of gas analyses, bacteriological and chemical investigations, and also by organoleptic analysis. Physical changes are not normally accompanied by gas formation or impaired odor or taste, and thus exhibit no evidence of decomposition. Chemical spoilage leads to the production of hydrogen; the product usually has in addition an unpleasant metallic taste but is not metabolized. Biological spoilage is characterized by carbon dioxide and the quality is greatly affected. In carbohydrate breakdown the pH level drops, while in protein degradation the pH level is higher than normal. A key for distinguishing between major types of spoilage was set up by Meyer (1956a); this can also be applied to heat-processed cans.
V. Chemical Processes

A. COLD MARINADES

Two phenomena obviously dominate the finishing process of cold marinades: (1) the acid reaction of the vinegar, which produces the tenderness so characteristic of marinades and largely due to proteolysis induced by autolytic tissue enzyme (Meyer, 1962a) and appearance of a broth-like taste by liberation of amino acids; (2) the effect of the table salt, causing removal of water and coagulation of protein. The salt at the same time inhibits the hydrolysis and causes it to proceed within desired limits. In addition there seems to be a third effect, namely, the aroma formation ascribed to microbial activities. If acetic acid and salt are added in considerably greater concentration, the microorganisms can no longer survive but the delicate aroma disappears.

Acetic acid acts as a hydrolytic agent, but above all as a preservative. It is supported in its preservative function by salt only in higher concentration, which is already very close to the maximum level compatible with an acceptable taste. Therefore a sharp distinction between chemical and bacteriological processes cannot be made in all instances. Our knowledge of the course of the finishing process is still very fragmentary from the scientific point of view, since it is most complex. Many studies will be required in order to clarify individual phenomena before a coherent picture will emerge of the over-all process. For example, essentially nothing is known in detail of how the hydrolysis of the fish flesh proceeds under the influence of acetic acid (but see Meyer, 1962a). Since these hydrolytic products may serve to enhance the development of microorganisms, this question is of particular significance. Since the beta-bacteria found in spoiled marinades decarboxylate arginine and glutamic acid, one or both of these amino acids must be formed during the acid hydrolysis. Similarly, whether the antagonistic action of salt is based only on the removal of water and/or coagulation of protein, or whether other factors contribute to inhibition of the hydrolysis, needs to be clarified.

As soon as the finishing bath comes in contact with the fish, a diffusion of acetic acid and salt takes place into the tissue of the fish flesh until a concentration equilibrium is reached. This proceeds relatively quickly. An equilibrium between vinegar and salt in the finishing bath and in the fish tissue is reached in about 24 hours, salt requiring slightly more time than acetic acid for full penetration. Nevertheless the complete finishing of the fish flesh, presumably due to a certain hydrolysis of the tissue, requires a somewhat longer time (Meyer, 1961b).

In following the fate of the acetic acid and that of the salt, the salt content of the final product is found to correspond rather closely to
theoretical estimates, whereas it is not possible to account in the same way for the final amount of acetic acid. This may be shown by an example. Herring with 65% water were placed at a ratio of 3:2 in a finishing bath of 5.6% acetic acid and 7.6% salt. If this acetic acid is divided between the water in the fish and in the brine and an equilibrium is reached, the theoretical acetic acid content in the finishing bath after treatment would be 2.82% acetic acid. But actually only 2.45% acetic acid was found, and thus 13.1% of the total acid was missing; these discrepancies are frequently larger. It is assumed that some acetic acid is bound to the protein, but this binding undoubtedly also depends on the amount of amines present in the fish tissue.

Assuming that the portion of acetic acid not retained in the aqueous phase is bound to protein, Wille (1948) calculated the amount of acetic acid bound in the fish flesh. He concluded from his experiments that the termination of the finishing treatment is dependent on the amount of acid bound in the flesh; at least 0.8% acetic acid should be present, whereas at 0.6% the fish is not finished. Since errors are easily introduced in view of the uncertainties in determination and calculation of this acetic acid content, the discrepancies referred to would appear to be less significant. One might equally assume that a certain defined amount of acetic acid would be a prerequisite for an acceptable finish.

Recent studies have contributed to the question of the acetic acid distribution in the softening process (Meyer, 1959, 1961a). It was observed that the traditional method of measuring acetic acid in marinades (extraction of the acetic acid with water at 100°C. (212°F.) and titration of an aliquot part of the clear solution with 0.1 N natron lye against phenolphthalein) gave far too high values due to buffering substances present in the tissue or due to the protein and its derivatives. The use of steam distillation made it possible to measure in quantitative terms the amount of acetic acid originally in the finishing bath and in the meat tissue. Furthermore, the acetic acid penetrates the fish tissue not only via its water, but is also attached to the protein although possibly as only very loose compounds.

From these distribution conditions, formulas were worked out by which it was possible to calculate in advance the amount of acetic acid \( E_1 \) required for raw marinades (compare Section III, A, 2). The required amount of acetic acid in a raw marinade with a ratio of fish to marinade of 7:3 is as follows:

\[
E_1 = \frac{E_2 \cdot [30 + 0.7 \cdot (H_2O + \text{protein})]}{30}
\]

where \( E_2 \) is the acetic acid content in the final finishing bath. Consequently the formula for a 3:2 ratio is:
5. MARINADES

\[ E_1 = \frac{E_2 [20 + 0.3 (H_2O + \text{protein})]}{20} \]

Such formulas can be set up for all other fish:marinade ratios. At least during the warm season, a value lower than 2.5% should never be allowed for \( E_2 \).

It can be proved with these formulas that with higher water content of the fish flesh, the acid content of the bath must be increased. Consequently in the example given (in Section III, A, 2), 3.5 kg. acetic acid is required at a tissue water content of 60% and protein 15%, while 3.8 kg. acetic acid is required for 100 kg. fish at a tissue water content of 70% and protein 16%. If herring with 10% difference in water content are put into finishing baths of equal strength, then a difference in acetic acid content of 0.2% is to be expected. Thus the differences are obviously not too great and it is therefore sufficient for practical purposes to calculate from the highest water content and the lowest fat content, respectively.

The fish in the finishing bath, lose about 15% of their original weight in the form of tissue water and soluble protein. Larger losses usually reflect spoilage or other defects in the flesh.

Vinegar content in the fish flesh (\( E_f \)) at the end of the bath treatment can be calculated according to the following formula, provided the acid uptake is due to a certain binding to the protein and loss of water from the fish tissue occurs:

\[ E_f = \frac{(L - d) \cdot E_2}{F - D} \]

where \( L \) is the original water content, \( d \) is protein, \( E_2 \) is the amount of acetic acid in the finishing bath when the treatment is terminated, \( D \) is loss in weight, and \( F \) is weight of the original fish. One practical example: Herring with 62% water and 16% protein were packed with a 2:3 ratio between the raw fish and the original finishing bath containing 7% acetic acid. A final acetic acid concentration of 2.5% is then to be expected in the final refining bath. The loss amounted to 14.7%. If we put these values into the formula, it reads:

\[ E_f = \frac{(62 + 16 - 14.7) \cdot 2.5}{100 - 14.7} = 1.9 \]

Values for \( E_2 \) of 2.53% and for \( E_f \) of 1.97% were found. When lower values are encountered in the final products it must be concluded that the finishing bath was of the wrong composition or that the acid content was reduced through bacterial action.
Hydrolysis of the fish flesh in the marinades is probably predominantly chemical in nature, since protein-degrading microorganisms are mostly acid-sensitive and therefore do not find a suitable medium for growth in marinades. To what extent autolytic enzymes play a role has not yet been clarified, although there have been a number of speculations on this point (Lücke, 1954). It was earlier thought that autolysis was less significant percentagewise. More recent investigations (Meyer, 1962a) indicate that the protein degradation to amino acids is largely a result of the activity of intrinsic enzymes. The acetic acid acts not so much hydrolytically as by creating an acid environment, in which cathepsin has its optimal range around pH 4.5. High concentrations of sodium chloride and of acetic acid tend to suppress hydrolysis, rather than the reverse. Amino acids from the fish protein are formed. These in turn are transformed in various ways by microbial activity when the acidity level allows such organisms to develop. The amino acids are largely decarboxylated, lysine to cadaverine, tyrosine to tyramine, arginine to citrulline and ornithine, glutamic acid to γ-aminobutyric acid, histidine to histamine, and ornithine to putrescine.

The hydrolysis is very temperature-dependent. At low temperatures just above the freezing point, the finishing treatment therefore takes a longer time than at the usual temperature of 10–12°C. This is important for the storage of merchandise ready for shipping. No appreciable losses take place in the cooler, but at higher temperatures it can be considerable. Finally, at very high temperatures the product becomes pulpy. This is noted in particular in incubator tests. Marinades at 37°C disintegrate to a very large degree because of autolytic hydrolysis, without being necessarily spoiled by microbial action. A temperature of 27°C is recommended for incubation in the laboratory, since disintegration by hydrolysis still remains within tolerable limits. Increased temperatures not only promote microbial activity but may also place at their disposal larger amounts of protein degradation products.

<table>
<thead>
<tr>
<th>Acetic acid content of brine</th>
<th>1.5%</th>
<th>1.0%</th>
<th>0.5%</th>
<th>0.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water in fish after 100 days (%)</td>
<td>66.4</td>
<td>71.45</td>
<td>71.70</td>
<td>77.80</td>
</tr>
<tr>
<td>Acetic acid after 14 days (%)</td>
<td>2.2</td>
<td>1.9</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Acetic acid in covering liquid after 100 days (%)</td>
<td>2.15</td>
<td>2.1</td>
<td>1.9</td>
<td>1.65</td>
</tr>
<tr>
<td>Brine after 14 days (pH)</td>
<td>4.10</td>
<td>4.10</td>
<td>4.15</td>
<td>4.20</td>
</tr>
<tr>
<td>Brine after 100 days (pH)</td>
<td>4.05</td>
<td>4.10</td>
<td>4.15</td>
<td>4.20</td>
</tr>
<tr>
<td>Shelf-life at 27°C. (days)</td>
<td>20</td>
<td>20</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>
5. MARINADES

As a cover brine a vinegar-salt solution of lower concentration than that of the final finishing bath is used. An example in Table I shows how analytical data are affected by different acetic acid concentrations in the brine. Herring, cut as a double fillet, at the end of the marination contained 59.3% water, 2.5% vinegar, and had pH 4.17. The fish:brine ratio was set at 2:1. It is apparent that the acetic acid content is lowered, the content of water raised, and the keeping properties as a whole reduced by too mild a brine (Meyer, 1962b).

**TABLE II**

<table>
<thead>
<tr>
<th>Age of spoiled marinade (days)</th>
<th>0</th>
<th>30</th>
<th>50</th>
<th>57</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid in brine (%)</td>
<td>2.2</td>
<td>2.0</td>
<td>1.24</td>
<td>0.94</td>
</tr>
<tr>
<td>pH</td>
<td>4.33</td>
<td>4.58</td>
<td>4.93</td>
<td>5.17</td>
</tr>
</tbody>
</table>

In spoiling cans, the amount of acid decreases and the pH value rises (Table II). The samples were taken from an experiment where different preservatives were used on the same product. Amines were formed from amino acids by gas-forming microorganisms, as will be seen below. These amines bind quantities of acetic acid, depending on their amount.

**B. COOKED MARINADES**

The preserving principle in cooked marinades consists in the combined effect of heat and acid in the bleaching bath; it is known that these two factors are more effective when acting jointly. There is a lack of investigations to support this conclusion under the conditions prevailing in marinades. The degree of acidity in the bleaching bath has no influence on the degree of acidity in the interior of the fish flesh, since the bleaching period is far too short to allow diffusion into the flesh (Meyer, 1953). Only surface action is involved. For this reason only a small amount of acetic acid is frequently present during treatment in the bleaching bath or when finishing in an incubator or air dryer. In the bleaching process, 15–20% of the weight, depending on the salt and acetic acid content of the bath, is removed from the product in the form of water. Thus the bleaching bath gradually becomes so diluted that it must be renewed from time to time.

An additional preserving effect is exerted by the acetic acid diffusing into the finished product from acid jellied brines so that an acid environment is created throughout the tissue, preventing the development of microbes. It is important to choose an acetic acid concentration high enough to produce within 24 hours a degree of acidity in the entire fish...
tissue that will prevent the growth of microorganisms. Diffusion from the jelly does not proceed as rapidly as in cold marinades and may be complete only after 8 days under certain conditions (Meyer and Kietzmann, 1958).

As in cold marinades, only a portion (about 15%) of the acid is used. The fish flesh has somewhat higher acid values than correspond to theoretical estimates. These additional amounts, small as they may be, are presumably bound via adsorption. The water content of the bleached raw product has some effect on the vinegar content of the flesh; 10% lower water content reduces the acetic acid content of the fish and raises that in the jelly by about 10% of its value. With 1.9% acetic acid in the original jelly and a raw product of 70% water, about 0.95% acetic acid is found in the jellied brine and 0.75% in the fish flesh at the end of the diffusion. These values are all considerably lower than the corresponding ones in cold marinades.

C. Fried Marinades

During frying, temperatures below the boiling point are reached in the interior of the flesh, although considerably higher temperatures prevail in the surrounding medium (Küchler, 1941). Understandably, these temperatures must remain lower as long as the fish still contain water. Only in the outer layers, particularly in the breaded layer, are higher temperatures reached; the flesh takes on a characteristic dark color and the typical aromatic components of fried products are formed. In the course of this process, the fish lose 20–30% of their weight in the form of water, depending on length of time, temperature, and thickness of the flesh or more correctly the relative surface. Herring, originally containing 67.2% water, 18.3% protein, and 12.6% fat, contained after frying 53.0% water, 26.5% protein, and 18.5% fat (Anonymous, 1950). The fried fish make up for this water loss to a very great extent during holding storage in the cover brine. But it must be kept in mind that the capacity for swelling is diminished due to the protein denaturation. In the example cited, the products increased in weight by 23% in 9 days. The absorption of water is thought to be independent of the particular vinegar and salt content of the brine. After 2–3 days, diffusion into the fried fish comes to an end. At the acetic acid concentration most commonly used, 2.5%, the final brine contained 1.3% and the fish flesh 1.2%; at an acetic acid concentration of 3.4%, the corresponding values were 1.8% in the final liquid and 1.6% in the fish flesh. If these values are compared with those of cold and cooked marinades, it is found that the acid content of the fried marinades lies between those of the other two.

In order to understand the various factors which influence the degree
of acidity in the final product, empirical figures frequently do not suffice, since the analytical values for the raw product exhibit wide variations. Therefore we have calculated theoretically, in Table III, the influence of water content on the degree of acidity of the finished product, in relation to the amounts in brine and in the fish flesh. The starting point was an

<table>
<thead>
<tr>
<th>Type of product</th>
<th>Water content (%)</th>
<th>Acetic acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>75.0 70.0 65.0 60.0</td>
<td>1.30 1.45 1.50 1.60</td>
</tr>
<tr>
<td>Fried</td>
<td>64.3 57.0 50.0 43.8</td>
<td>1.00 0.95 0.90 0.85</td>
</tr>
<tr>
<td>Finished</td>
<td>70.6 65.0 59.4 53.6</td>
<td></td>
</tr>
</tbody>
</table>

acetic acid concentration of 2.5% in the starting bath and a fish:liquid ratio of 1:0.8, a frying loss of 30%, and a reabsorption of water to the extent of 23%.

If these calculated values are compared with those found in practice, the actual percentages of acetic acid once again are lower in the brine and higher in the fish flesh than the theoretical data indicate. It is possible that the higher values in the fish flesh are again due to adsorption. It has not been taken into account in this table that with a low water content of the herring there is at the same time a high fat content. Herring with a high fat content lose considerable amounts of fat during frying; it is probable that this causes an automatic increase in water content of the fried product. There appear to be no investigations on this particular point.

VI. Microbiological Processes

The microbial aspects of marinades are poorly studied. Investigations started immediately prior to World War II were interrupted, but have been resumed in the postwar period.

According to Aschehoug and Vesterhus (1943), *Pseudomonas* and *Achromobacter* species and flavobacteria are the most commonly encountered microorganisms in freshly caught fish, herring in particular. Most of these species have proteolytic properties. They are acid-sensitive and not likely to be found in marinades, since pH values around 4.5 prevent their development. Only spore-formers, primarily from the *B. subtilis* group, are found frequently in lower dilutions, especially if the acid inoculum is first neutralized. Schönberg and Lochmann (1955) hold
these spore-formers responsible for damaged products. According to preliminary investigations by the author, spore-formers cannot develop in the acid environment of the marinades but survive because of their spore form. Kreuzer (1957a), on the basis of studies on marinades inoculated with spore-formers, also came to the conclusion that these organisms cannot generally be considered the cause of such spoilage. He leaves open the possibility, however, that in marinades maintained under mild acid conditions they may aid in causing spoilage. The significance of heat in the fried and cooked marinades in terms of microorganisms has already been indicated. Nevertheless, heat does not kill off all germs, in particular not the nonspore-formers. This phenomenon is known from the milk and other industries. In any case heat has some debilitating effect, since fried and cooked marinades are more durable than cold marinades at the same acetic acid concentration. The possibility cannot be excluded that other factors may also play a role. It should be added that the risk of recontamination is not as great with fried and cooked marinades, since they are not processed intensively after heating. Cold marinades, by contrast, are in frequent contact with the bacteria-rich dressing tables as they are worked up further.

In microbiological studies the bacterial count by the Koch plating procedure is usually employed. There are many uncertainties in this procedure; in particular, only those bacteria are counted for which the correct nutrient medium was by chance employed. Other bacteria, which may well be of decisive importance, may escape detection completely. Moreover, a change in microflora may make it necessary to change the nutrient media. This is rigorously required in the investigation of marinades and will have to be taken into consideration in future investigations.

In experiments on marinade preparations, to give an example, the author worked up a raw product herring with a bacterial content of $85 \times 10^3$ g. on broth gelatin and $12 \times 10^3$ g. on wort agar. If finishing was carried out properly, no beta-bacteria, to be discussed below, appeared within 10 days, with the exception of a few spore-formers; however, this was not so if the bath was too weakly acid. Bacterial development was observable after 70 days, even at stronger concentrations of vinegar; its extent was inversely proportional to the acid concentration. The number of bacteria in this case decreased relatively on neutral media and increased on acid media. These investigations have not been completed; but we conclude that the original flora is more or less pushed back by an acidophilic flora which was possibly never present in the raw product. In any case, Kreuzer (1957a) has isolated organisms which degrade glutamate with gas formation from marinades prepared under
conditions protecting them against secondary infections. But since he obtained no spoiled products in marinating experiments on the ocean, he also believes that the content of acidophilic forms takes place through contamination on land or in the hold of the ship (Friebe, 1962).

A. COLD MARINADES

1. Beta-Bacteria Spoilage

In spoiled marinades, Meyer (1956b) found the Betabacterium buchneri group in predominant amounts; these organisms liberate CO₂ from the amino acids arginine and glutamic acid by decarboxylation and could be considered the cause of the damage. This involved heterofermentative lactic acid bacteria, which in the acid range present in the marinades can meet their metabolic needs from these amino acids in the absence of carbohydrates. Kreuzer (1957a) has confirmed these results. Beside these beta-bacteria, there are other heterofermentative lactic acid bacteria not yet identified and whose metabolism has not been elucidated. They are not capable of attacking glutamic acid with the nutrient media used so far.

Beta-bacteria have been isolated not only from cold marinades but also from fried marinades and several specialties related to the cold marinades. In fried marinades these spoilage phenomena are not as pronounced, since there are only small amounts of free amino acids.

A study was made in laboratory experiments, using pure cultures, of various conditions affecting this group of bacteria, particularly the influence of temperature, pH, salt, various acids, and various preservatives (Meyer 1956b, c). The temperature optimum is 30–37°C. According to Buttiaux (1954), there are beta-bacteria with a growth minimum at 4°C. Salt has a slight inhibitory effect but only at concentrations above 6.5%. The minimal pH value appears to be specific for each acid or, rather, the pH value as such is not as determining a factor for the inhibition as the acid itself, since for example a pH value below 3.0 is still tolerated in weakly buffered nutrient solutions containing hydrochloric acid, while in acetic acid medium the lower pH limit lies at 4.0. Of decisive importance are the concentration and specific inhibitory action of the acid used. In this regard acetic acid, on the basis of its large buffering capacity, has proved superior to all other acids studied, such as lactic, citric, citraconic, or tartaric. Molds, which actually can play a role in marinades only in open containers, are also inhibited most strongly by acetic acid. The question whether better keeping characteristics are achieved by acetic acid than by fermentation vinegar or vice versa has not been resolved. Fermentation vinegar is given preference by some on the grounds of possibly having a somewhat better aroma.
In the decarboxylation of amino acids by beta-bacteria, the corresponding degradation products (gamma-aminobutyric acid, among others) raise the pH value and gradually tie up the acetic acid (cf. Table II). In weak finishing baths or with herring which stick together in the bath, beta-bacteria may cause neutralization of the acetic acid via degradation products, before the marinating acid penetrates the fish flesh. This may lead to formation of undesirable red spots in which an elevated pH value is encountered; such marinades are condemned.

It is of interest that the beta-bacteria are capable of diacetyl formation. One may conclude from this fact that under certain conditions a part of the typical aroma of the marinades is derived from the activity of these otherwise undesirable organisms. In support of this we may cite the findings (p. 179) that the fine aroma disappears in the finishing bath because of too high vinegar and salt contents. The broth-like taste of the marinades may be caused by gamma-aminobutyric acid, formed from glutamic acid by decarboxylation.

2. Preservatives

Among the common preservatives, only hexamethylenetetramine has proved effective, even at low concentrations (10–25 mg./100 g.). With benzoic acid and sorbic acid as well as dehydroacetic acid, concentrations are needed which are near the solubility limit of the substances in question. Since in marinade preparation, preservatives can be added to the brine only in the aqueous phase, 2–3-fold amounts are required. But with these preservatives this cannot be done technically.

For the antibiotics (penicillin, aureomycin, streptomycin, terramycin, and nisin), the required concentrations are higher by a factor of about 10 than that of hexamethylenetetramine (Meyer, 1957). The antibiotic nisin from starter cultures appears promising, but extensive technical investigations are needed in order to establish its effectiveness. In marinating practice, higher amounts of hexamethylenetetramine (about 25 mg. per 100 g.) are needed than is indicated by the threshold value in experiments in vitro (5–10 mg.). This is related to the fact that an appreciable portion of the hexamethylenetetramine is bound by the fish flesh (Hutschenreuter, 1956). Kreuzer (1957b) reports the relation between temperature and the elimination of formaldehyde from hexamethylenetetramine in marinades. He found the level of hexamethylenetetramine to remain above this threshold value for a sufficiently long time, only if the product is stored in the cold.

The question whether a smaller amount of preservative may be added, if the initial bacterial content is low than if it is high, is answered in the affirmative by Kreuzer (1957). Meyer (1957) answers it in the
negative on the basis of investigations carried out at 37°C. On theoretical grounds, he considers it unlikely that differences in the initial bacterial content can play a decisive role. The problem requires further clarification.

3. Miscellaneous

Kreuzer (1957a) studied the influence of a combination of salt and sucrose; at a salt concentration of 7%, a sugar concentration of 15–20% was necessary to achieve satisfactory growth inhibition. Inhibition of glutamic acid decarboxylation takes place at lower concentrations.

In the use of glutamic acid or spices containing glutamic acid, caution is needed since overdosage can lead to spoilage. The threshold value for gas development from glutamic acid is about 0.3% (Meyer, 1956b). Since in general it is not known how much glutamic acid is already present in the marinades, this addition should not go above 0.1%.

4. Keeping Tests

For the prognosis of keeping quality, Wille and Kühlmorgen (1951) has proposed the determination of a microbial growth factor. This is nothing more than a running assessment of the increase or diminution of the bacterial count. But as was stated, this is based on the assumption of a uniform microflora and the use of suitable nutrient media.

Kreuzer (1953) bases a prognosis of the keeping properties on the course of the titration curves in the final finishing baths. This procedure does not appear to stand a strict test. The characteristics of the titration curves depend on various factors, such as protein hydrolysis products and possibly their microbial degradation products. Similar effects could conceivably be coincidental and depend on entirely other factors.

B. Cooked Marinades

In jellied products, contamination with nonmotile gram-positive rods about 5–6 μ in size was very frequently observed in earlier days; these rods gave rise to lens-shaped colonies in gelatin (Moll, 1929). According to Struve (1929), this contamination could be counteracted by the addition of hydrogen peroxide, by stronger vinegar concentrations, and in particular by the use of high grade gelatin; such contamination no longer occurs.

In cans with cooked marinades, inadequately sealed or incompletely filled, there is an occasional growth of molds, *Penicillium* species. These organisms may develop as soon as they have access to a sufficient amount of oxygen. Such contamination can be traced externally by the so-called shaking test, in which case the contents of the can are no longer firmly
fixed. It can easily be avoided by greater care in filling and sealing of cans.

An alleged instance of botulinus poisoning renewed consideration of the question to what extent forms of Clostridium botulinum can develop or produce toxins in the acid medium of marinades. The most important types of this organism, in terms of growth and toxin formation in vitro in nutrient solutions with different pH values and in cooked marinades with jellied brine of varying acetic acid concentration, have been investigated (Meyer and Kietzmann, 1958). A pH of 5.3 was the lower limit for development.

To a final pH value of 5.1 in the finished product, a corresponding level of 0.9% acetic acid prevails. But since at this concentration diffusion into the center of the fish flesh requires more than 7 days, germs present in the interior of the flesh still have a good opportunity to grow. Botulinus organisms can grow well within 24 hours; therefore, the acid concentration must be high enough so that within 24 hours the pH is definitely below the minimum of 5.3. This is achieved at acid levels above 1.95%. By keeping the product cool, the development of bacteria can be suppressed until the acid diffusion is complete. Gelatin may possibly be a source of infection and must therefore be checked bacteriologically in every instance.

C. Fried Marinades

Fried marinades are sometimes spoiled by ropy microorganisms. The product becomes encased in slime and is less suitable for consumption. Küchler (1942) isolated spore-formers of the B. subtilis group believed to be causative. Slime formation seems to occur only when contamination is introduced after the frying, and originating in the breading. It is therefore recommended that the breading operation be partially separated from the packing of the fried products. It cannot be concluded from this study whether filament formation was caused only by pure cultures of spore-formers. But it is obvious that other negligence in manufacture may cause this or similar disturbances. Most spore-formers are susceptible to acids.

VII. Improved Shelf-Life; Preservatives

The principal cause of spoilage of cold marinades is, as stated above, the heterofermentative lactic acid bacteria. In fried marinades, slime formers appear; in jellied products, proteolytic microorganisms and others may occur. The technical measures against proteolytic organisms and probably also against slime formers is a sufficiently high content of acetic acid, combined with a corresponding amount of salt. Special precautions need
to be taken in order to avoid contamination of fried and cooked marinades.

It is more difficult to avoid spoilage by lactic acid bacteria. Their suppression requires high acid concentrations, in some instances exceeding what is permissible from the point of view of taste; a too marked taste of vinegar and salt can indeed be covered by suitable spices and saccharin but only to a certain degree. An important factor in assuring the shelf-life of marinades is the temperature during storage. The optimum for growth of the lactic acid bacteria is 30°C. Below this level, the development of these organisms is delayed but not prevented. Marinades stored at cooler temperatures (4–6°C.) keep a long time, but as soon as they are stored for any length of time at higher temperatures approaching the bacterial optimum, a development of these lactic acid-producing organisms is to be expected. With the use of hexamethylenetetramine and cold storage, the risks of spoilage are minimal (cf. p. 188).

Among the preservatives, only hexamethylenetetramine seems to be effective in checking microorganisms. There is, however, considerable objection to its use from a medical point of view because of the possibility of formaldehyde formation, unless it can be shown that the small amounts needed for preservation are safe for human consumption. The use of sorbic acid, dehydroacetic acid, and the esters of p-hydroxybenzoic acid is hindered from the technical standpoint by their low solubility in water. The use of benzoic acid is further vitiated by the unpleasant taste it gives to the product if added at levels adequate for preservation. Only nisin seems to offer a feasible alternative.

The legal aspects of the use of preservatives will not be discussed here. But it should be noted that in this respect legislation differs from country to country.

The chief prerequisite for the manufacturing of a high quality marinade is the use of high grade raw materials. Every change in their composition affects the marinating process in one way or another. The need for meticulous cleanliness during the entire preparative process is also self-evident. This holds equally true for the containers, working tables, and implements and, not the least, all the ingredients.

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