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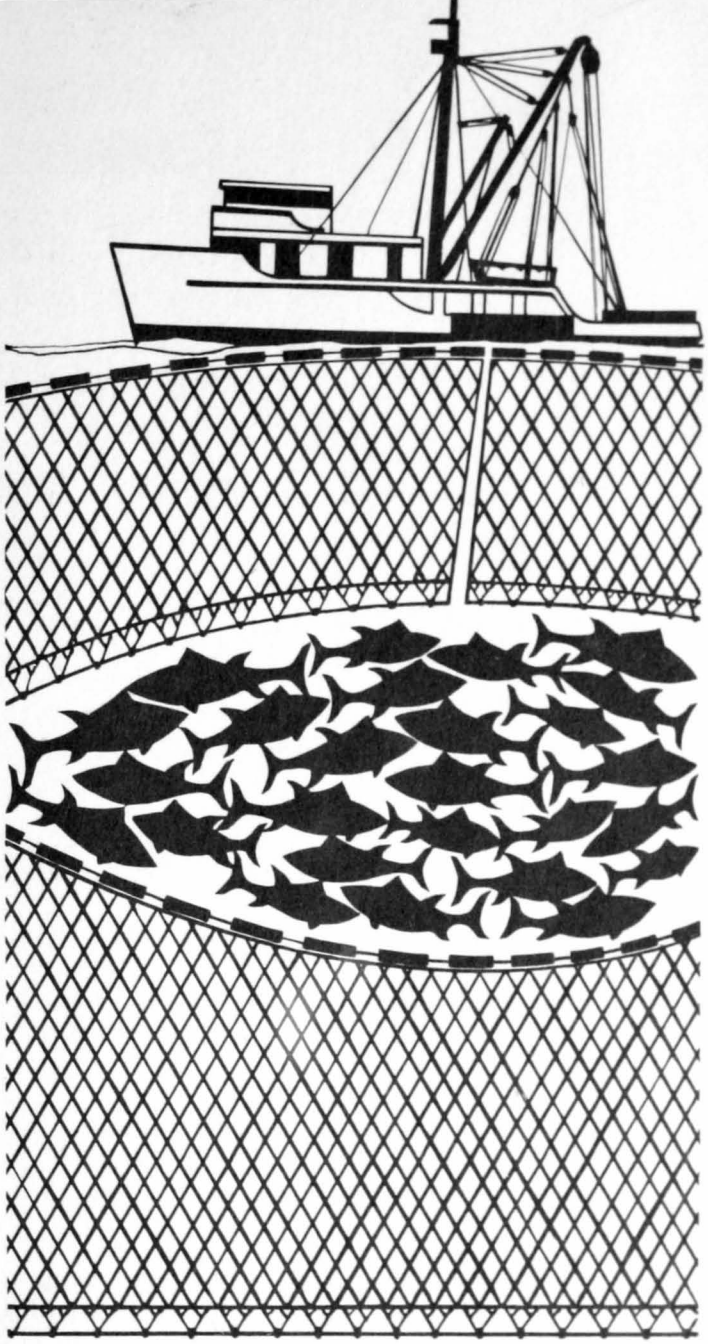

FISHERY INDUSTRIAL RESEARCH

VOLUME 6 NO. 1

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FISHERY INDUSTRIAL RESEARCH

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As the Nation's principal conservation agency, the Department of the Interior has basic responsibilities for water, fish, wildlife, mineral, land, park, and recreational resources. Indian and Territorial affairs are other major concerns of America's "Department of Natural Resources."

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COMMERCIAL FEASIBILITY OF IRRADIATING HADDOCK AND COD FILLETS: INTRODUCTION

by

John D. Kaylor and Edward J. Murphy

ABSTRACT

In the studies introduced by this report, three questions were asked: Is a high enough proportion of haddock and cod, as landed in New England, fresh enough to justify their being irradiated? (2) Is the temperature of fish during commercial distribution by common carrier sufficiently low to preserve the quality of the fish? (3) Can haddock and cod fillets be irradiated and shipped on a commercial scale and still exhibit a significantly increased shelf life at iced temperatures? The data collected in the studies indicate that the answer to each of the three questions is "yes."

Glass and Smith (1960)[1] have shown that irradiating food with radioactive cobalt-60 at sterilizing dose levels of 4.5 to 5.6 million rads does not impart radioactivity to the product. In the irradiation preservation of fresh fish, the dose levels used are far below sterilizing levels -- generally less than 300,000 rads. Thus, when fresh fish are preserved by irradiation, they do not become radioactive, so radioactivity is not a problem.

Nickerson, Lockhart, Proctor, and Liciardello (1956) and Carver and Steinberg (1959) have shown that the irradiation of fresh fillets significantly extends the shelf life of the fillets under laboratory-controlled conditions. Although this finding is encouraging to the businessman who might be interested in preserving fish by irradiation, it does not tell him whether the shelf life of fresh-fish fillets irradiated on a commercial scale at low-dose levels of irradiation and shipped under commercial conditions will show an increase that is commercially significant. In short, before a businessman would invest his money in this process, he would have to be shown that the favorable results in the laboratory can also be realized on a commercial scale.

To investigate the feasibility of irradiating and shipping fishery products on a commercial scale, the Atomic Energy Commission has built and the Bureau of Commercial Fisheries has staffed the Marine Products Development Irradiator at Gloucester, Massachusetts (Kaylor and Slavin, 1965).

Although we would like to use this commercial-sized irradiator to investigate the irradiation of all commercially important species of fish, we have had to choose a few species to study initially. Because haddock and cod

[1] R. A. Glass and H. D. Smith. 1960. Radioactive isomer production in foods by gamma rays and X-rays. Stanford Res. Inst. Contract DA19-129-QM-1511. Quartermaster Food and Container Inst., Chicago, Ill., 66 pp.

Authors: John D. Kaylor, *Supervisory Food Technologist*, and Edward J. Murphy, *Food Technologist*, Bureau of Commercial Fisheries Technological Laboratory, Emerson Avenue, Gloucester, Massachusetts 01930.
Published February 1970.

are the most important species in the New England groundfish industry, they were the logical choices.

Until the early 1920's, the fishing industry marketed haddock and cod in the round, but since then, it has marketed them in the form of fillets, owing to the greater demand for fish products in this convenient-to-use form.

Unfortunately, the shelf life of the fillets is short. Kaylor (1966) and Daniel Yankelovich Incorporated (1966) found that the shelf life seldom exceeds 5 days at the retail level. This short shelf life precludes distributing the fillets widely by common carrier, the only way that they can now be transported and still be sold at a relatively low price.

The market for fresh New England groundfish fillets thus is limited to the area shown in Figure 1. If the shelf life could be extended, the market, of course, could be enlarged correspondingly. The New England groundfish industry would then benefit from this larger market, and the people in the new marketing area would, in turn, benefit by being able to choose from a wider variety of fresh fish.

The purpose of the work reported here, therefore, was to determine whether it is feasible to irradiate haddock and cod fillets on a large scale and then ship them by common carrier to distances well beyond present-day markets and still maintain the fillets at a high level of freshness.

We carried out this work in three investigations. These studies were of such a nature that if the first had turned out to be unsuccessful, we would not have undertaken the second, and if the second had turned out to be unsuccessful, we would not have undertaken the third.

To operate, an industry needs, of course, a supply of suitable raw material. Unfortunately, irradiation, like other means of preservation, such as freezing, does not improve the

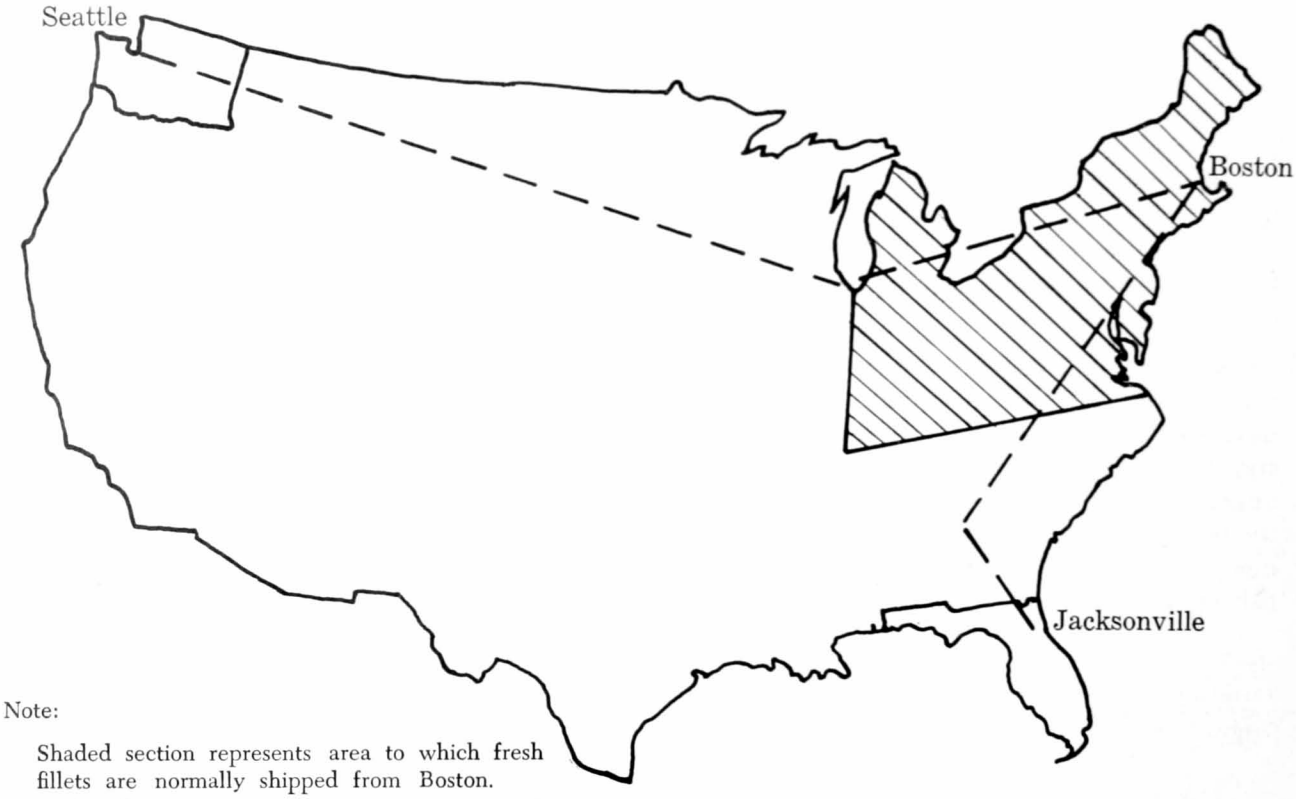

Figure 1.—Map showing routes of shipping studies.

freshness of fish. It merely helps to preserve whatever freshness is present. Furthermore, economics will not permit the industry to irradiate fish of questionable quality. Accordingly, the purpose of the first study was to determine whether a high enough proportion of haddock and cod, as landed, is fresh enough to justify being irradiated.

Fortunately, we could simplify the study. Haddock and cod are handled similarly, so that general conclusions concerning the freshness of one species will apply to that of the other. Historically, Boston, which is located near Gloucester where our irradiator is, has been a leader in the haddock fishery. These facts led us to choose haddock as the species to be studied and Boston as the port in which to study them. The first investigation in the series therefore was to determine the proportion of haddock landed in Boston that are fresh enough for irradiation.

This study showed that 78 percent of the haddock landed was of a level of freshness that will justify treatment by irradiation. Thus, the proportion of haddock and cod suitable for irradiation is more than adequate.

After we found that supply is not a problem, we had to find the temperature patterns of fresh fillets during commercial distribution via common carriers. If these temperatures turned out to be high, the commercial shipment of irradiated fishery products probably would be unsuccessful. Our second study showed, however, that the average temperature of fillets in interstate commerce was less than 40° F. Thus, temperature during shipment via common carriers is also not a problem.

Having now found that supply and temperature during transit are not problems, we had to learn whether haddock and cod fillets could be irradiated and shipped on a commercial scale and still exhibit a significantly increased shelf life at iced temperatures. This final study showed that, under commercial conditions, haddock and cod had an extension of shelf life of 10 or more days longer than the nonirradiated control samples. This extension is great enough to enable industry to ship fish to any sector of the nation and still have enough residual shelf life to permit marketing in the normal manner.

The details of the three studies will be reported in three future papers.

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MS. #1969

RECOMMENDATIONS FOR HANDLING AND ICING FRESH PACIFIC HALIBUT ABOARD VESSELS

by

Wayne Tretsven and Harold Barnett

ABSTRACT

The icing of halibut aboard the fishing vessel sometimes is inadequate to minimize the loss of quality during the trip. Observations made of icing and other handling practices aboard halibut vessels serve as the basis for the recommendations suggested here for improving the method of handling. Adhering to these recommendations will help the fisherman land halibut of more uniform quality.

CONTENTS

INTRODUCTION

During the 5 years 1962 through 1966, some of us at the Bureau of Commercial Fisheries Technological Laboratory at Seattle, Washington, evaluated the quality and condition of Pacific halibut landed at ports in Alaska, British Columbia, and Washington. When the fishing vessels were unloaded, we occasionally noted that the halibut showed an excessive loss of quality and that this loss of quality was more serious among the small halibut than among the large ones. We also noted that these small halibut usually had little or no ice in their pokes (the poke includes the mouth cavity and the visceral cavity), whereas the large halibut ordinarily contained at least some ice. In addition, we noted in the summer that the

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vessels, which usually brought in halibut of good quality, occasionally landed halibut of poor quality because of inadequate icing. One other thing we noted was that the methods of handling the halibut greatly influenced their quality.

These observations prompted us to study factors involved in the handling and icing of halibut. The purposes of this article are to report our findings and to give recommendations that will increase the effectiveness of the handling and icing of halibut and will thereby help to ensure that the consumer will have halibut of uniformly high quality.

Because the quality of halibut is so closely related to the method of icing used, you can tell much about the quality of halibut simply by observing how well they have been iced. In the following discussion, we consider first the factors that affect the handling and icing of halibut and then the factors that indicate the quality history of halibut.

I. FACTORS THAT AFFECT THE HANDLING AND ICING OF HALIBUT

Factors that affect the icing of halibut include (A) the size of the poke and the density of the ice used and (B) other factors -- such as: (1) the temperatures of the halibut, of the ice, and of the surrounding and (2) mechanical refrigeration.

A. SIZE OF POKE AND DENSITY OF ICE

Halibut are a relatively large, thick-bodied fish having good storage qualities; however, when stored in ice, undesirable discolorations of the white skin (Figure 1) and indentations

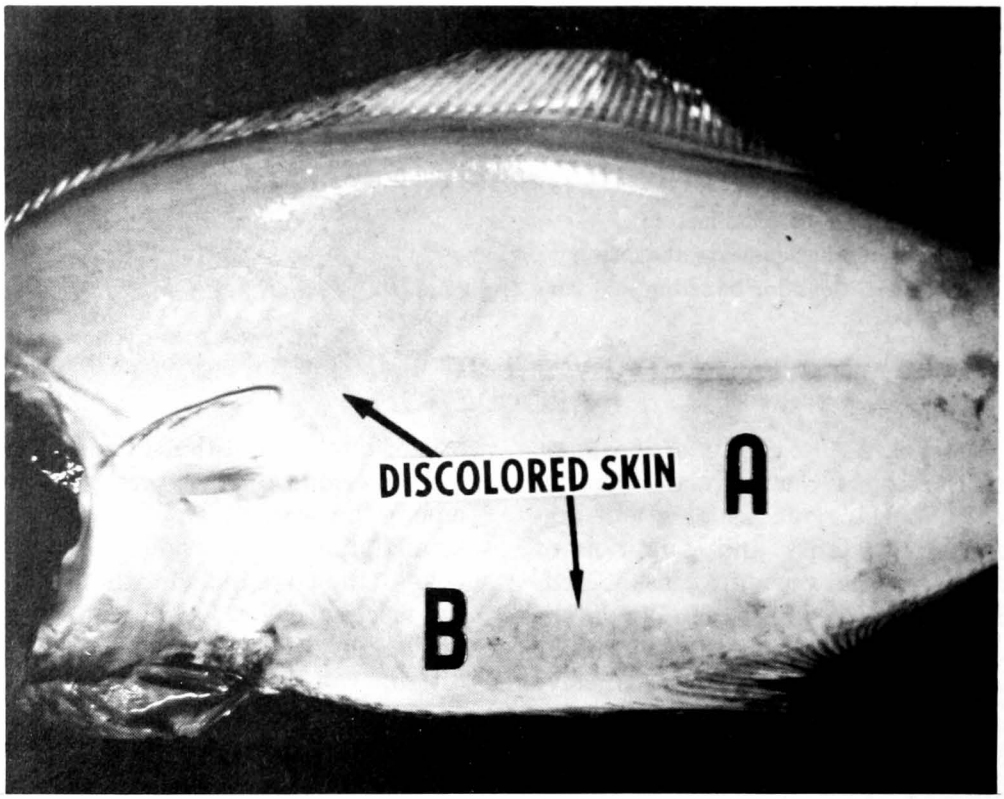

Figure 1.—Fresh halibut showing: (A) a white skin area that had been in direct contact with other halibut and (B) a discolored "yellowing" area due to aerobic growth of *Pseudomonas fluorescens*.

(Figure 2) due to particles of ice may occur. The discoloration is a "yellowing" or "greening" and is due to the growth of *Pseudomonas fluorescens,* a motile bacterium that grows on the slime at low temperatures in the presence of free oxygen.[1] The discoloration is on areas of the skin where oxygen is available, as in the proximity of pieces of ice or open spaces, and it doesn't occur where oxygen isn't available.

Special techniques have been developed to overcome these undesirable conditions. Emphasis has been directed toward filling the poke with crushed or flake ice and toward limiting the amount of ice distributed between and around the halibut to only that which will melt and provide adequate chilling without any pieces of ice remaining to cause discoloration or indentation of the skin. Instead of icing halibut on shelves where they would be exposed to oxygen, the halibut are now iced and packed tightly in pens to exclude the presence of oxygen. As in the icing of other fishes, however, a layer of ice is used to keep the halibut away from the sides of the hold and away from the bottom of the hold, and ice is applied to the top of the load.

Except for the top layers of halibut, the iced halibut are usually placed on their side with the dark side down and the white side up. Small hemorrhages and bruises that objectionably affect the appearance of the white side tend to disappear when the halibut are iced in this position.

For economic reasons -- primarily, the time and labor required -- some fishermen do not attempt to ice the pokes of the small halibut as well as they do those of the more valuable large halibut. Unfortunately, however, when small halibut spoil, they contribute to an increased rate of spoilage of the entire lot.

[1] F. C. Harrison. 1929. The discoloration of halibut. Nat. Res. Counc. Can, pp. 214-239.

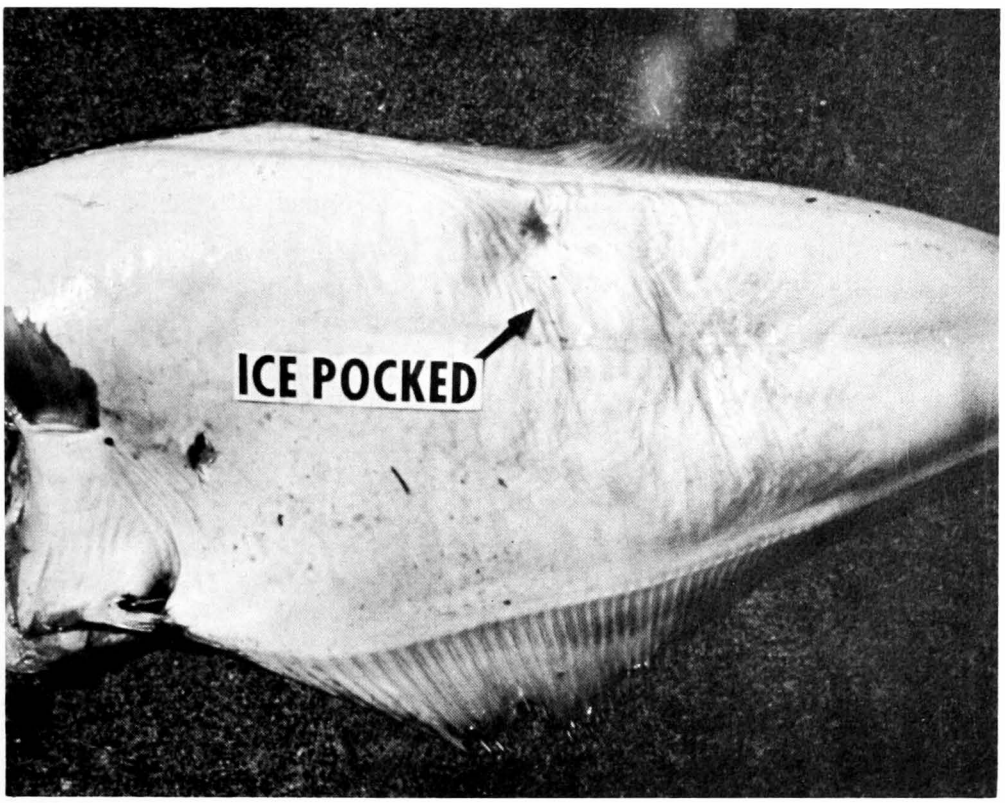

Figure 2.—Fresh halibut having "ice pocks"--that is, indentations caused by particles of ice between iced fish.

Because we found that inadequate icing was associated primarily with the smaller halibut, we studied the icing of halibut of various sizes to find why the smaller ones were sometimes poorly iced.

We assumed that the size of the poke is proportional to the size of the halibut and, hence, that the amount of ice that can be packed in the poke is also proportional to the size of the halibut. Bell (1966),[2] in discussing poke size, commented on factors that affect the ratio of weight of viscera to the weight of halibut, and he stated: "The observed individual variation has been from a minimum of 6 percent to about 27 percent maximum." His data indicate that the poke represents a slightly greater portion in large halibut than in small halibut.

We found variations in both the size of the poke and the shape of the poke among halibut of similar weight in our sampling of commercial halibut. Halibut of various sizes caught in July near Goose Island, which is about 75 miles north of Vancouver Island, were quite plump and had relatively small pokes that represented about 16 percent by volume of the whole halibut. On the other hand, those caught in November in the Bering Sea were big-bellied halibut whose pokes represented 22 percent of their volume. In general, we found that the size of the poke is proportional to the size of the halibut and that the poke represents about 18 percent of the volume of the whole halibut.

When the poke is iced, the sides of the head and body walls bulge, thereby permitting more ice to be added to the poke. In spite of this bulging, the amount of ice that can be packed into the poke is, of course, limited by the size and shape of the poke. With smaller halibut, bulging of the body wall is more limited than it is with larger halibut, and proportionately less ice can therefore be packed into the pokes of small halibut. On a weight basis, the ice equalled about 17 percent of the weight of the large halibut and only about 6 percent of the weight of the small halibut.

[2] H. F. Bell, Director of Investigations, International Halibut Commission, Seattle, Washington, private communication, March 30, 1966.

The bulk density of the commercial crushed ice and flake ice obtained at various times and locations during this study varied considerably. It ranged from 28 pounds to 39 pounds per cubic foot. As the amount (weight) of ice in the poke is affected by the density of the ice, the use of low-density ice may contribute to inadequate icing. The amount of low-density ice that can be packed into the poke of a small halibut may not be enough to chill the halibut adequately.

B. OTHER IMPORTANT FACTORS

We consider first such handling factors as stunning, bleeding, cleaning, removing body heat, and draining away melt water and then consider mechanical refrigeration.

1. Handling Factors

During our study of temperatures aboard commercial halibut vessels, we simultaneously observed the handling practices aboard the vessels. On some vessels, the method of handling caused the halibut to lose quality.

a. Halibut that had not been stunned often bruised themselves when struggling on deck. Dressed halibut were frequently bruised (Figures 3 and 4) by being dropped into the hold.

b. Halibut were not always bled adequately. (Bleeding results in halibut of a lighter, more desirable, color.)

c. Halibut were not always cleaned adequately.

d. Halibut were sometimes purposely left on deck for as long as several hours, because the fishermen believed that the body heat should be dissipated before the halibut are chilled with ice in the hold.

e. Incoming iced halibut sometimes lay in melt water in the pens, because the water had accumulated faster than it had drained out.

After finding that the internal temperatures were higher in small halibut lying on deck than

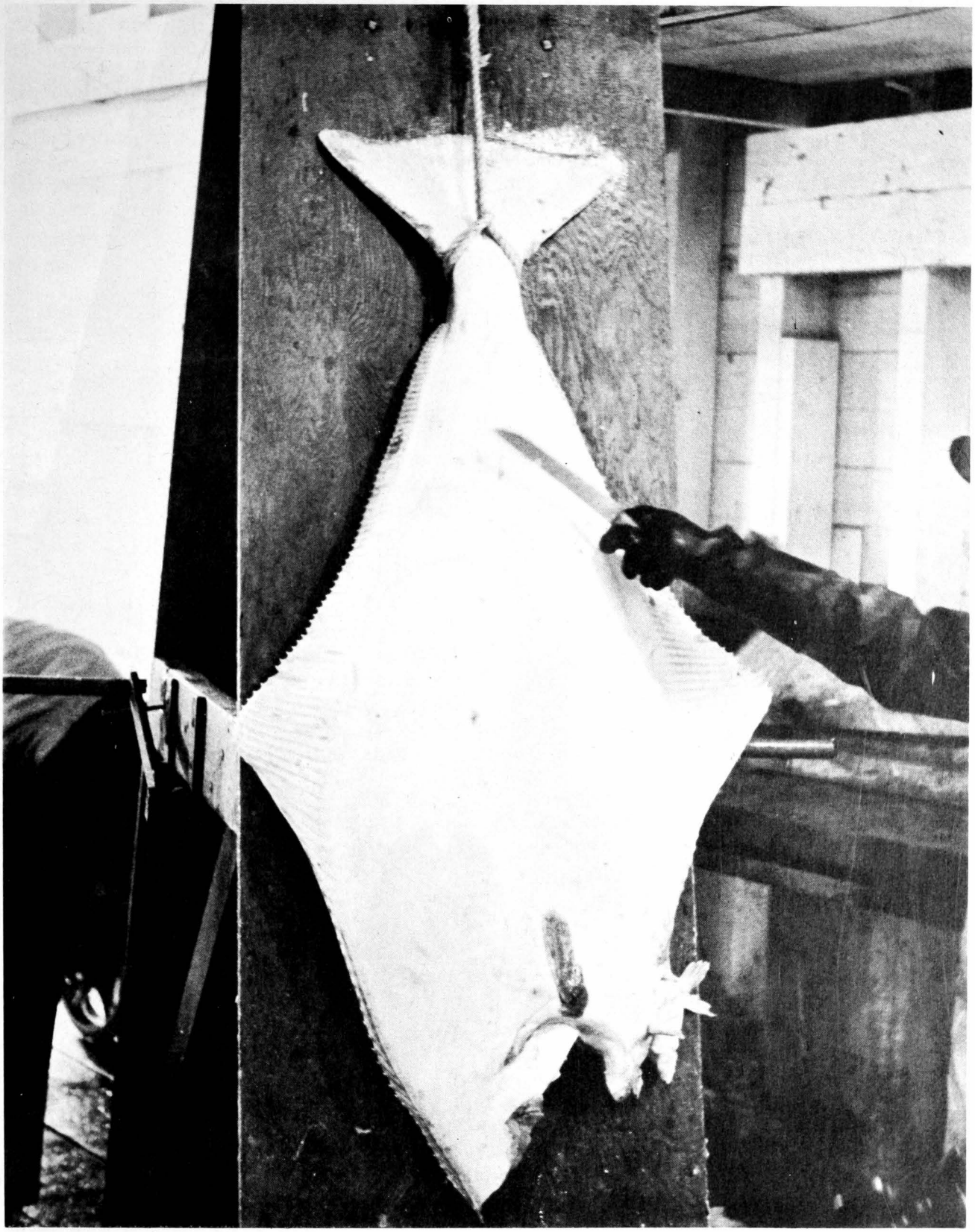

Figure 3.—The knife held by the fletcher indicates where an internal bruise occurs. The bruise was caused by the halibut being dropped from the hatch onto ice.

Figure 4.—An internal bruise caused by dropping the halibut onto ice.

in larger ones, we studied temperature in greater detail.

The internal temperatures of halibut caught on adjacent hooks on the same line or on nearly adjacent hooks were determined at the following times: (a) immediately after the halibut were landed on the deck; (b) after they lay on the deck 6 hours; (c) after they were iced 24 hours; and (d) after they were iced 48 hours.

Table 1 shows that immediately after the halibut were landed on the deck, the internal temperature of the small halibut was 4° F. higher than that of the large halibut. This difference in temperature applied to halibut brought to the surface by a gurdy operating at full speed -- that is, at 146 feet per minute. Lengthy delays in pulling in the line caused the temperature of the halibut to approach more nearly that of the surface water. This finding applied both to large halibut and to small ones.

Changes in temperature occur more rapidly, however, in the smaller halibut. This fact is reflected in the more rapid rate at which they deteriorate in quality, and it emphasizes the adverse effect of holding them at a relatively high temperature for even a short time.

Allowing the temperature of halibut to rise by leaving them on deck should therefore be avoided. Not only does the quality of the halibut deteriorate rapidly when their temperature rises, but both more ice and more time are then required to chill the halibut adequately. Thus, from the standpoint of both quality and economy, the temperature of halibut should be kept from rising.

Aged ice is sought by halibut fishermen because they believe that it preserves the halibut better than freshly made ice does. Aged ice is usually kept in cold storage, where it is gradually cooled considerably below its melting point. Aged ice is usually available at the start of the halibut season but is seldom available during the summer, when spoilage is more of a problem. Undoubtedly, the favorable reputation of aged ice is due to its lower temperature making it easier to handle and last longer.

Table 1.—Internal temperatures of halibut aboard a fishing vessel

Time of temperature measurement	Internal temperature of halibut weighing:			
	18-22 lbs.	27-32 lbs.	38-44 lbs.	76-84 lbs.
	°F.	°F.	°F.	°F.
Immediately after the halibut were landed on the deck	48	47	47	44
After the halibut had lain 6 hours on deck	67	66	64	57
After the halibut had been iced for 24 hours	34	34	35	36
After the halibut had been iced for 48 hours	33	33	33	34

Note 1: The vessel was fishing near the Queen Charlotte Islands, August 1966. The temperature of the water was 43° F. at the bottom and 54° F. at the surface. The ambient air temperature was 70° F.
Note 2: The internal temperature of the halibut was determined by inserting a thermometer into the center of the body, with the bulb of the thermometer at the thickest part of the body.

Use of colder ices in sufficient quantities can chill halibut to temperatures below 32° F., and holding at the lower temperatures can result in retaining quality for a longer time. Most research workers advocate the use of ice at its melting point because it is at this temperature that it absorbs the most heat. In addition, water from the melting ice is probably useful in washing slime and bacteria from the fish.

Storage at temperatures lower than that of melting ice, however, permits fresh halibut to be stored for longer times with less loss of quality due to bacterial action and to loss of fluid from the flesh than when the halibut are stored in melting ice. With mechanical refrigeration, fresh halibut can be maintained at temperatures of 29° F. to 32° F.

If mechanical refrigeration is used, care must be taken not to lower the temperature of the halibut below 29° F., its initial freezing point. Otherwise, problems may be encountered in unloading the frozen halibut.

Most fishermen, in attempting to control the temperature of the halibut, dress them and put the dressed halibut into the hold as soon as possible. As a number of halibut are accumulated in the hold before they are iced, some of the halibut undergo a slow and limited prechilling before being iced. Prechilling by immersing the dressed halibut in slush ice, refrigerated sea water, or refrigerated brine is recommended because the chilling is not only

rapid but the prechilled halibut can be stowed with less ice, thereby permitting the stowage of more halibut in the same space.

Considerable ice (refrigeration) is required to dissipate the heat that enters the hold. Insulating the bulkheads, the sides of the hold, and top of the hold; flooding the deck with sea water; and placing barriers such as curtains at the opening of the hatch are means of reducing the infiltration of heat to keep the temperature from rising unduly.

2. Mechanical Refrigeration

Mechanical refrigeration is used in most halibut vessels primarily to reduce the amount of ice required and thereby permit larger payloads. In addition, colder temperatures can be attained, which can result in halibut of better quality and of increased keeping time. Mechanical refrigeration is used effectively by (a) prechilling the hold before ice is taken aboard, (b) chilling and keeping the ice at a lower temperature, and (c) keeping the iced halibut at 29° F.

II. FACTORS THAT INDICATE THE HISTORY OF ICING

Because fresh-water ice melts and refreezes at 32° F., its condition within iced halibut indicates how well the halibut have been chilled and stored. Loose and dry particles of ice with little or no evidence of melting and of freezing indicate that the halibut were maintained at a temperature below 32° F. and that the ice used has melted little or not at all, owing to its initial low temperature or to the prechilling of the halibut, or to both. Dry clumps of ice indicate that the ice melted partially, probably during the chilling of the halibut, followed by freezing of the ice due to the lower storage temperatures attained by mechanical refrigeration. Clumps composed of large aggregates of ice indicate that more ice has melted and resolidified than do clumps composed of many small particles of ice. Ice in a melting condition (Figure 5) indicates temperatures of 32° F. or higher, and if the ice is dirty, is discolored, and has a foul odor, it indicates that the quality of the halibut has probably deteriorated. When little or no ice is present, the halibut have been inadequately iced or have been held for too long a time. Under these circumstances, the halibut could have spoiled.

RECOMMENDATIONS FOR HANDLING AND ICING FRESH HALIBUT

1. Stun and bleed the halibut as they come aboard the vessel.
2. Immediately after bleeding them, dress and clean them inside and outside.
3. Keep the temperature of the halibut from increasing.
4. Immediately after cleaning each halibut, slide it down a chute into the hold; do not bruise it by dropping it.
5. Prechill the halibut.
6. Ice the pokes of all halibut--small halibut as well as large ones.
7. Lay iced halibut with the dark side down and the white side up.
8. Because the pokes of small halibut are often iced inadequately, use additional ice around the small halibut. (Note: To risk discoloration of the skin resulting from the use of the ice around the halibut, which permits the growth of aerobic bacteria, is better than to risk spoilage of the flesh.)
9. Use ice of high density and low temperature.
10. Use mechanical refrigeration to lower the temperature of the hold before obtaining ice; maintain the iced halibut close to 29° F., but do not allow them to freeze.
11. Use thermometers placed throughout the hold to measure the temperature.

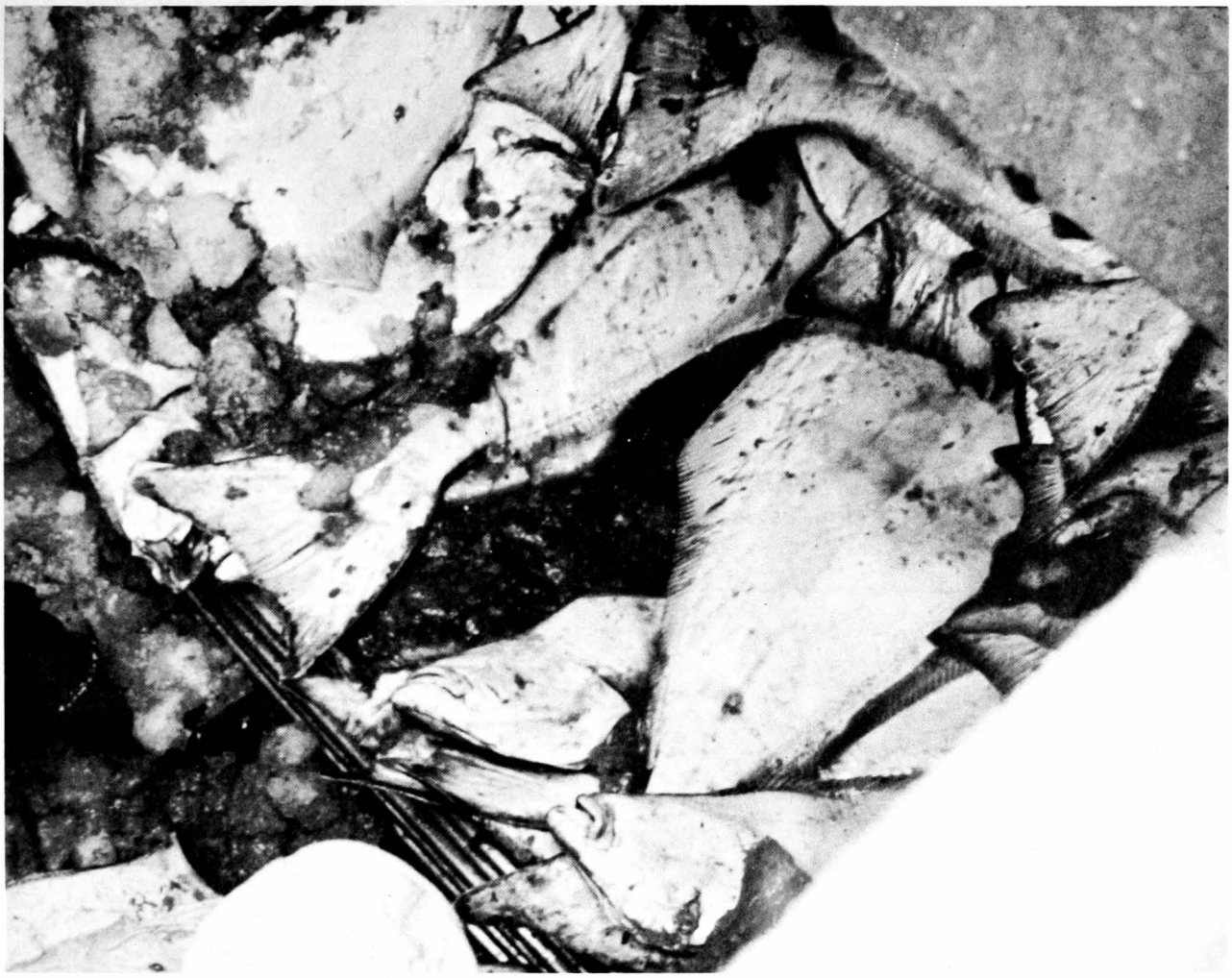

Figure 5.—Halibut in dirty, discolored melting ice.

12. Use more ice in warm weather than in cool weather.

13. Reduce the amount of heat entering the hold by using effective insulation, by providing curtains as heat barriers about the chute leading from the hatch opening to the ice, and by flooding the deck with sea water.

14. Provide drainage facilities throughout the pens and the holds to prevent blood, slime, or melt water from accumulating and from thereby contaminating the halibut.

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PHYCOCOLLOIDS

by

Norman W. Durrant and F. Bruce Sanford

ABSTRACT

Although phycocolloids--gelatinous materials produced from seaweeds--are economically important, they are not widely known materials. This paper discusses the three principal phycolloids manufactured in this country--namely, agar-agar, algin, and carrageenan --and outlines the ways they are produced and the ways they are used. At the manufacturer's level, these three phycocolloids are worth about 15 million dollars a year to the United States.

CONTENTS

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INTRODUCTION

Algae have been classified in several ways. One common way is to divide them into four major classes on the basis of their color--*Chlorophyceae* (green algae), *Cyanophyceae* (blue-green algae), *Phaeophyceae* (brown algae), and the *Rhodophyceae* (red algae). The green and blue-green algae usually grow in fresh water, whereas the brown and red algae are found almost exclusively in marine habitats. These latter are the algae usually referred to as seaweeds. Of the four classes, the brown and the red marine algae provide the principal products of commerce.

The main commercial value of seaweeds lies in the products derived from them by chemical treatment. In the past, these products have included a wide variety of materials, such as iodine, acetone, and various minerals (Sanford, 1958). Owing to competition from other more economically practical sources, however, these materials are no longer derived from seaweed in this country. The major seaweed products manufactured in the United States today are those that have the ability to form gels and colloidal suspensions--that is, the phycocolloids (Idson, 1956; Whistler and BeMiller, 1959). The term "phycocolloid" comes from two Greek words, *phykos*, meaning seaweed, and *kolla*, meaning glue. The last part of the term derives from one of its physical characteristics.

Although the phycocolloids are strategically and economically important, they are not widely known materials. The purpose of this article, therefore, is to discuss these important marine products derived from our seaweed industry.

For the purpose of this article, phycocolloids are divided into two main groups: those of minor economic importance and those of major economic importance.

I. PHYCOCOLLOIDS OF MINOR ECONOMIC IMPORTANCE

The phycocolloids of minor importance include laminaran and fucoidan from brown algae as well as funoran from red algae (Whistler and BeMiller, 1959). A far larger number of these minor phycocolloids could be manufactured if an economic use could be found for them.

Laminaran, which, as the name would lead one to suspect, comes from *Laminaria*, a genus of kelps. Laminaran, a polysaccharide with starchlike properties, can be used in the production of a soluble surgical dusting powder. Sodium laminaran sulfate may find use as a blood anticoagulant; hydroxyethyl laminaran, as a plasma substitute.

Funoran is a gluey material obtained principally from funori, the dried matter prepared by the Japanese from *Gloiopeltis*. Funori has long been used in the Orient for sizing textiles --it is the pasty substance applied to cloth as a glaze or filler.

Several other derivatives have been isolated from seaweed, but they are primarily laboratory curiosities that have little commercial importance at present.

II. PHYCOCOLLOIDS OF MAJOR ECONOMIC IMPORTANCE

The principal colloidal products made from seaweed are agar-agar, algin, and carrageenan (Figure 1). These products are used in foods, pharmaceuticals, and industrial materials.

To place the colloidal products industry in economic perspective, we first look into the economic value of the major phycocolloids; then we consider each of the phycocolloids individually.

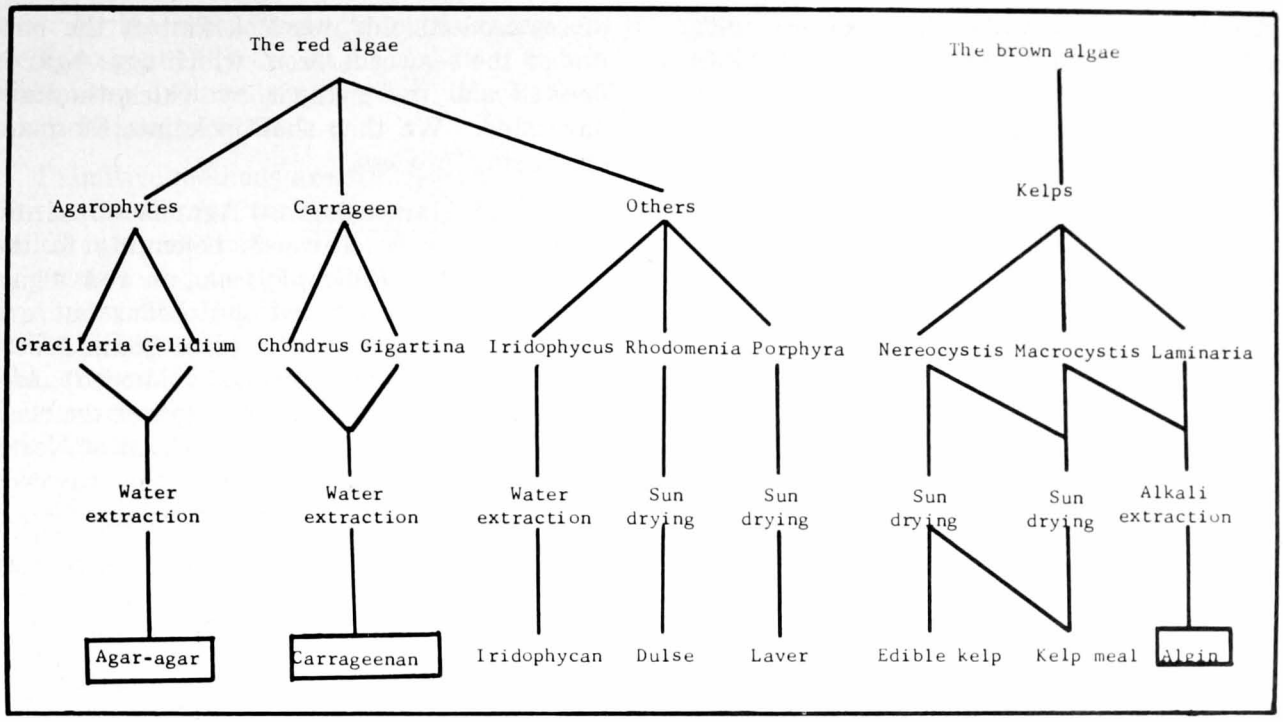

Figure 1.—The commercially important seaweeds of the United States and the primary products (including food, etc.) derived from them.

A. ECONOMIC VALUE OF THE MAJOR COLLOIDS

U.S. seaweed processors produce nearly 15 million dollars worth of agar-agar, algin, and carrageenan each year. These seaweed colloids compete with colloids derived from other sources--for example, gelatin, methyl and carboxymethyl celluloses, starches, pectin, and various industrial gums. Some of the newer synthetics, such as polyvinyl-pyrrolidone, polyoxyethylenes, and polyacrylamides, also compete with phycocolloid products in the United States (Idson, 1956; Whistler and BeMiller, 1959).

When prices of seaweed colloids are compared with those of other colloidal materials, seaweed products appear to be at a disadvantage, especially in the food, pharmaceutical, and cosmetic fields. Algin and carrageenan cost about 1 to 2 dollars a pound; agar-agar, about 4 dollars a pound. Prices per pound for competitive material are roughly 1 dollar for gelatin, 75 cents for cellulose ethers, 50 cents to 1 dollar for various tree gums (arabic, karaya, and tragacanth), and 15 to 20 cents for starches. When used, however, seaweed colloids often prove more economical than do lower priced competitive materials for two reasons. First, small amounts go a long way. Second, they often have special properties that the competitive products do not have.

There are many examples of special properties of seaweed colloids. Carrageenan and algin products have invaded the market and are now useful stabilizers for ice creams and chocolate milk. Agar-agar now is unchallenged as a gelling agent in bacteriological media. Other important uses for seaweed extractives will be discussed in detail later.

Certain nonseaweed materials occupy, through traditional usage, almost impregnable positions in food fields. Pectin, an extract of fruit peel, is traditionally used in making household jelly. Gelatin, which is obtained from animal matter, is the gelling agent primarily used in making most clear desserts and marshmallows. Carboxymethyl cellulose and methyl cellulose, both of which are derived from cellulose fibers, are widely used in dietetic bulk foods and laxatives. Starches from potatoes and cereals lead in the pudding

market, and casein-phosphate (from milk) leads in the instant-pudding field (Idson, 1956).

B. MAJOR PHYCOCOLLOIDS CONSIDERED INDIVIDUALLY

Having considered briefly the economic value of the three major phycocolloids--agar-agar, algin, and carrageenan--we now consider each of them individually, in detail.

1. Agar-Agar

We consider first the production of agar-agar and then its use.

a. Production. — Because harvesting is one of the critical determinants in the economics of seaweed colloids, we look first at the habitat of the seaweeds from which agar-agar is derived and the methods by which they are harvested. We then shall look into the manufacturing process.

(1) Harvesting. — Agar is obtained from red-purple seaweeds belonging to the botanical class *Rhodophyceae*, or red algae. They grow in nearly all the oceans but are gathered mainly off the coasts of South America, North America (primarily Mexico), and Africa. Unfortunately, only a few of the class contain agar. Along the West Coast of North America, the most prevalent of the seaweeds containing agar is *Gelidium cartilagineum*.

Usually, agar-bearing seaweeds (Figure 2)

Figure 2.—On the left, a bed of *Gelidium cartilagineum*, one of the principal seaweed species used in the manufacture of agar-agar.

grow on the ocean floor at depths rarely exceeding about 150 feet. In the turbulent waters where they ordinarily grow, they attach themselves to rough rocks.

Primitive methods are still used to harvest the seaweeds for making agar. Some are pulled into rowboats with rakes or gathered by waders at low tide. Others are collected by divers; SCUBA diving is the most common method (Figure 3). In Mexican waters, from whence most of the seaweed for U.S. agar production comes, the divers wear head-to-toe pressure suits and helmets (Figure 4).

The divers frequently live and work the entire season, which comprises all but two of the winter months, in isolated camps on offshore islands. From the base camp, the diver and his helpers ride to the seaweed beds in a pango, or diving boat. By using a diving helmet, he can stay down from 1 to 4 hours. About 1,500 pounds of wet weed represents a good day's work (Figures 5 and 6). Experienced divers claim that octopi, moray eels, barracuda, and sharks are not troublesome; the real dangers, they say, are the sharp rocks, swells, and bottom currents that can cut or snap an air hose or a lifeline.

After being brought ashore, the seaweed (Figure 7) is sun-dried, baled, and shipped to the processing plant.

(2) Manufacturing. — Once the baled seaweed has arrived at the processing plant, the many steps in the extraction and purification of agar begin (American Agar and Chemical Company, San Diego). Rigid chemical, physical, and bacteriological control is maintained (Figure 8) for several reasons. The raw material varies from batch to batch, yet the final product must be uniform. Because agar is chemically sensitive, it is subject to subtle variations and reactions; yet the requirements of the U.S. Pharmacopeia--as well as those of the Armed Forces, the industries, and the laboratories, where the agar will be used--must be met or exceeded. Hence, a host of the sea's minerals and other substances that constitute impurities must be removed.

Figure 3.—Divers preparing for underwater harvesting of *Gelidium cartilagineum*.

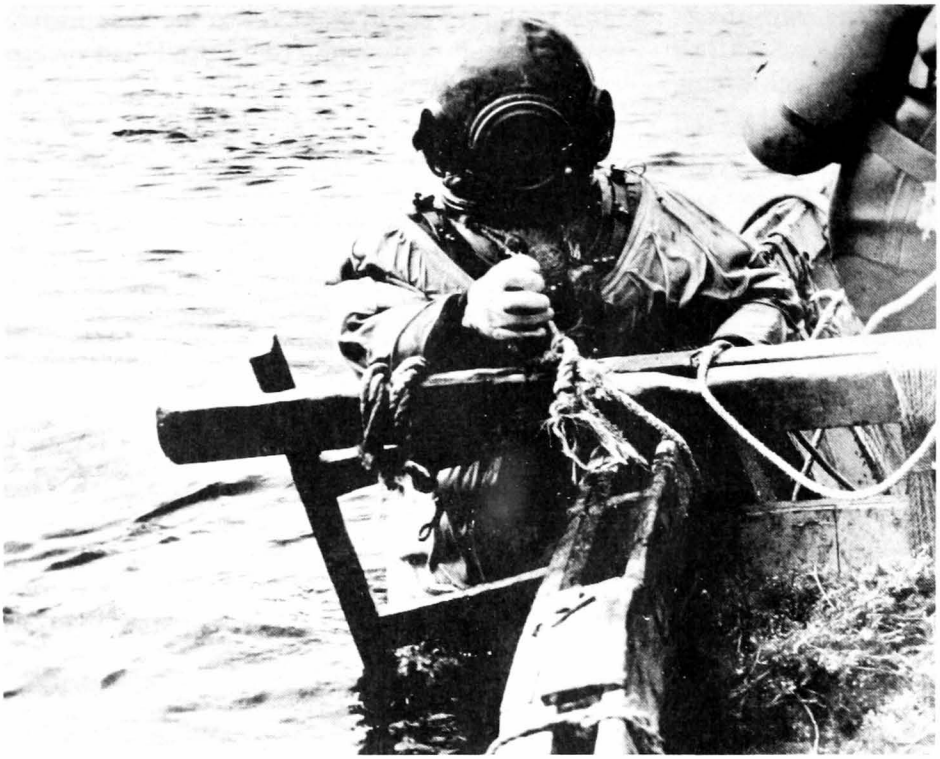

Figure 4.—Diver in pressure suit.

Figure 5.—Diver with an armful of *Gelidium cartilagineum*, illustrating the laborious method of harvesting.

Figure 6.—A netful of *Gelidium cartilagineum* from the ocean floor being dumped in the boat.

Figure 7.—*Gelidium cartilagineum* being spread on the beach to dry.

Figure 8.—Examination of gel sample as one step in the rigid control of quality.

The impurities are removed in eight steps:

1. The seaweed is thoroughly washed (Figure 9) to remove such palpable matter as foreign gums, sea salts, and calcareous incrustations and shells. This preliminary processing may take up to 2 days.

2. The seaweed is placed in large autoclaves or pressure cookers (Figure 10) and cooked with water until the agar-containing matter is separated from the fiber.

3. When the extraction is complete, the liquor (the solution of agar in water and the soluble impurities) is poured into sedimentation tanks (Figure 11). Here more of the impurities are precipitated and then are removed by filtration.

4. The remaining liquor is pumped into long sterilized trays where it congeals into sheets of firm, dark-colored, raw agar gel.

5. The gel is frozen and held at a subfreezing temperature for several days (Figure 12). Because the agar itself is insoluble in cold water, certain of the impurities will go into the ice and leave the agar behind. The ice is later melted, and the impurities are washed away.

6. The relatively pure agar is washed again, bleached, sterilized, treated (Figure 13) for removal of the small amount of remaining impurities, and washed yet again.

7. All the free water is removed from the agar by suction (Figure 14), leaving an

Figure 9.—Seaweed being washed and chemically treated to remove various gums and minerals.

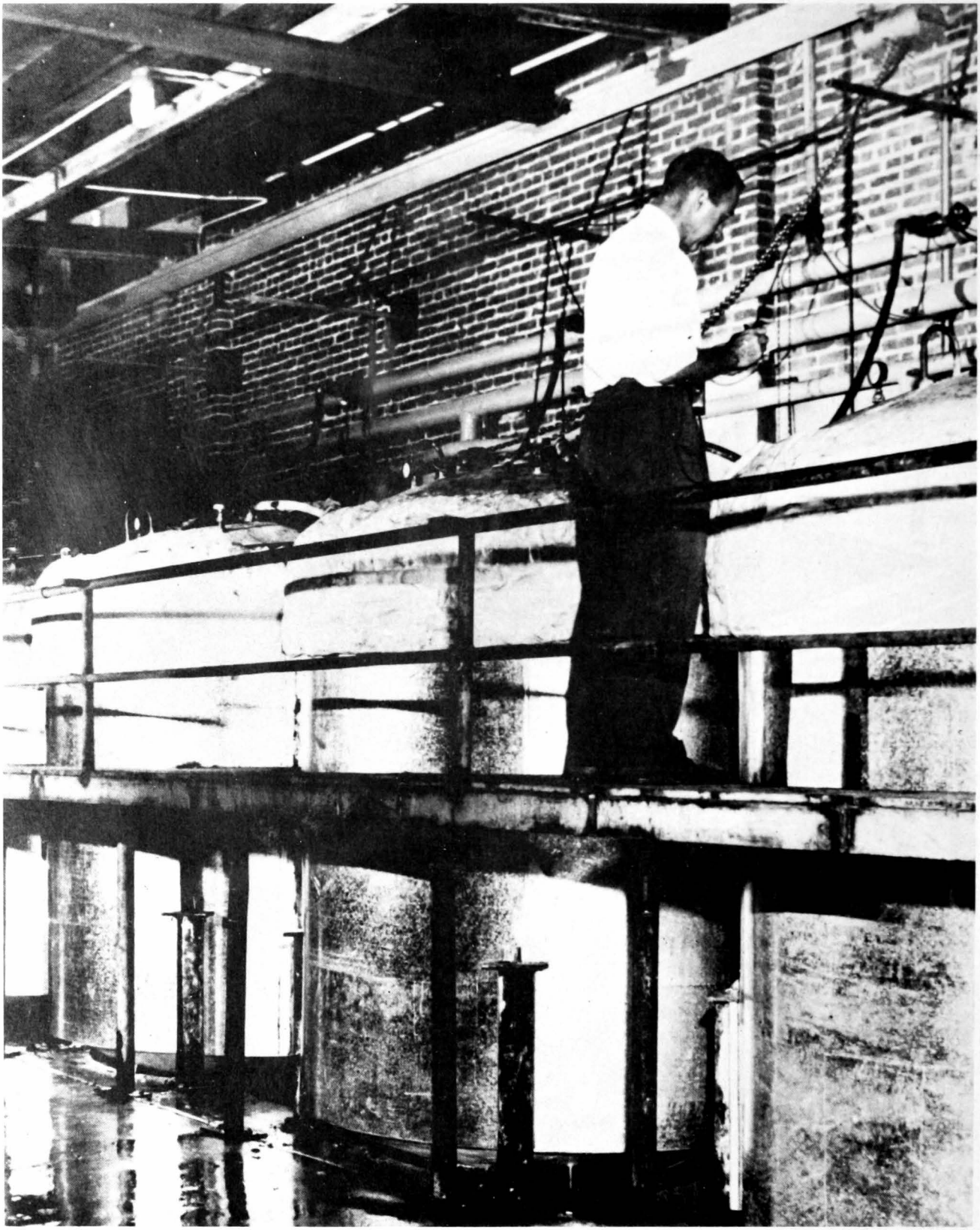

Figure 10.—Autoclaves for cooking the seaweed to separate the agar-containing matter from the fiber.

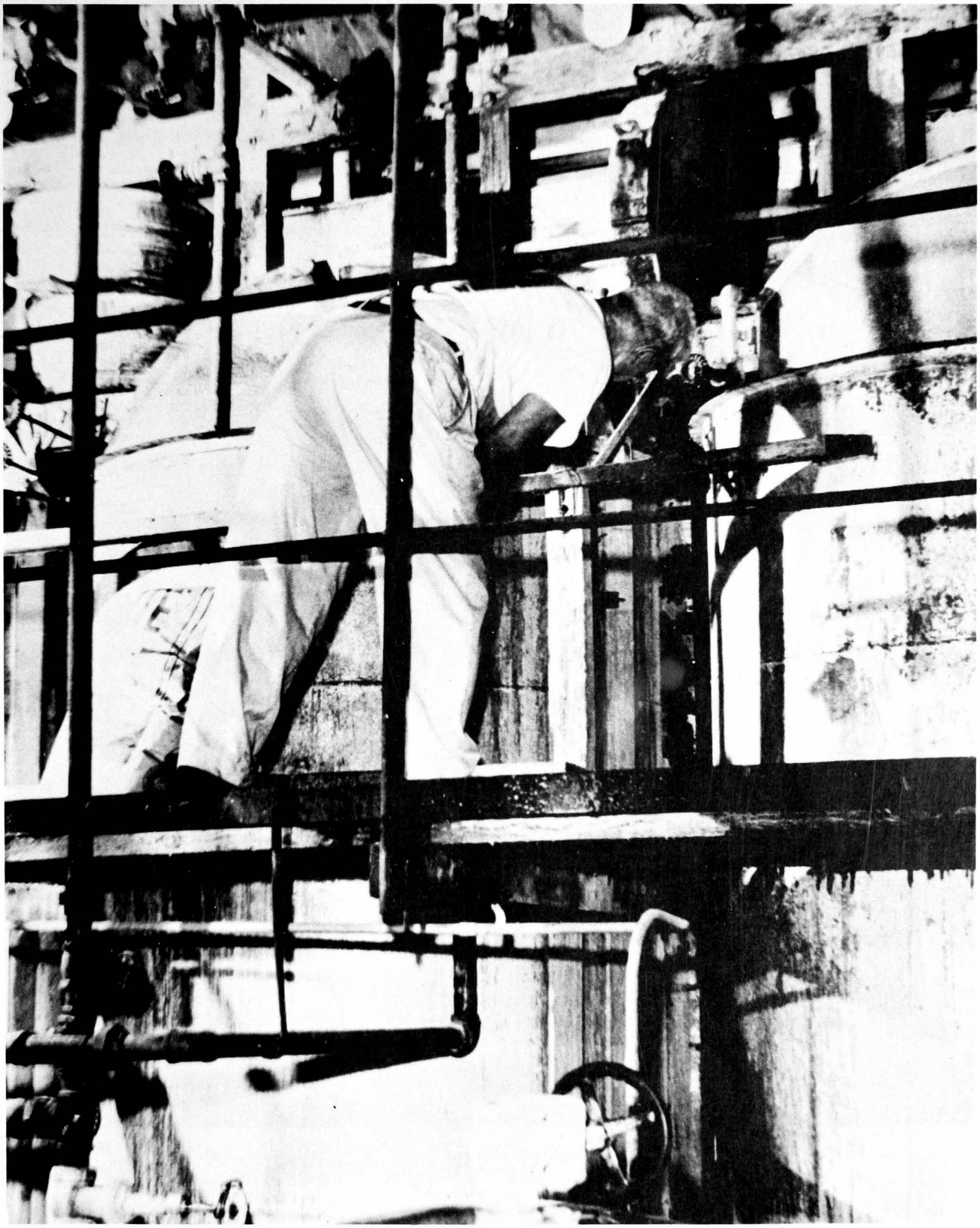

Figure 11.—Sedimentation tanks for the removal of impurities from the agar.

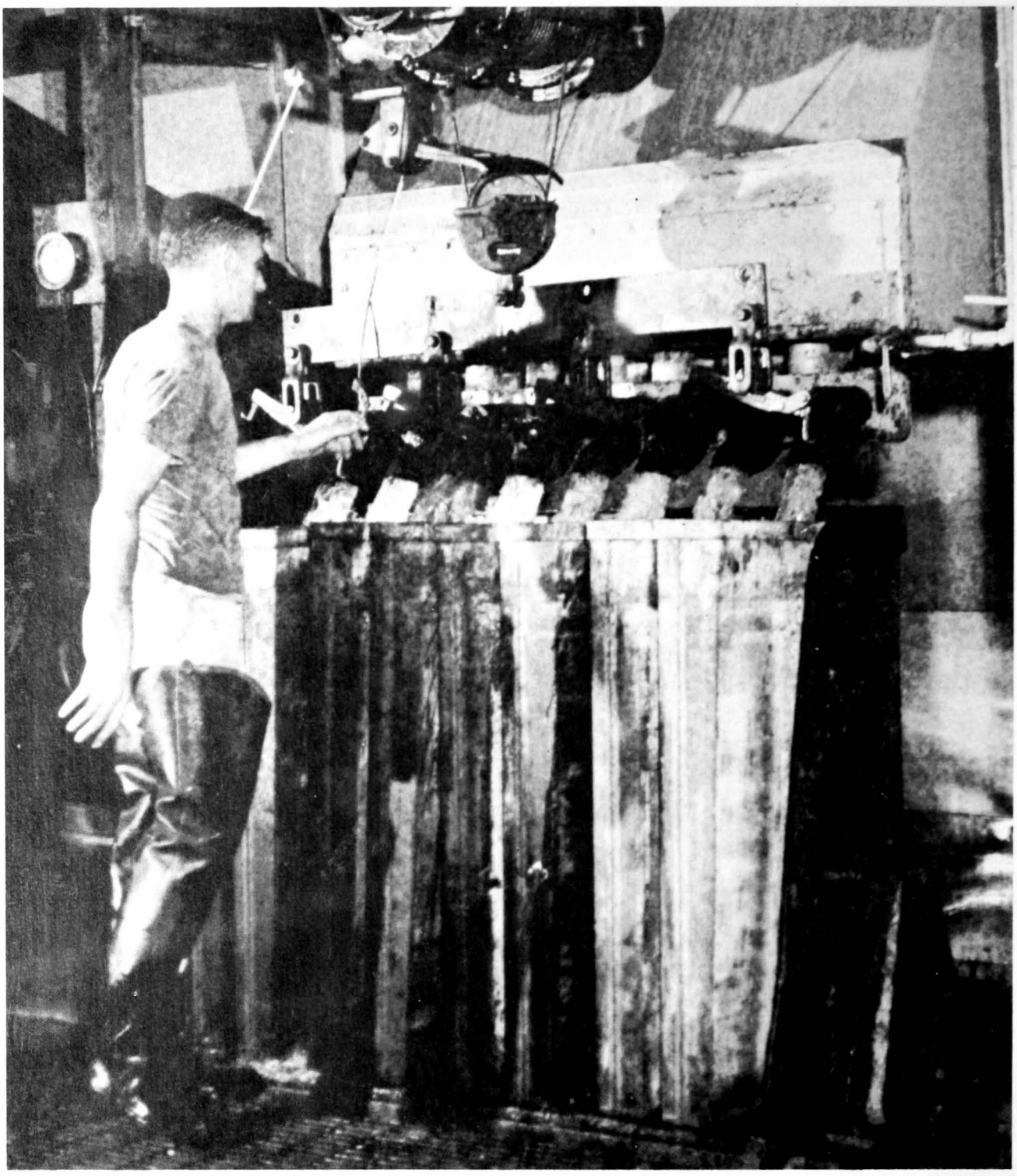

Figure 12.—Gel being frozen--an important step for removing water-soluble impurities.

Figure 13.—Additional washing for removing impurities.

Figure 14.—Removal of water from agar by suction.

odorless, tasteless substance that is practically white.

8. The flakes are literally thrown from heated metal tanks into long fingers or socks of white nylon through which hot air at 250° F. passes continually. The purified agar flakes are now ready for packaging (Figure 15) and marketing.

a. Use.—Because the uses of agar are inextricably bound to its attributes and qualities, we look at the properties that determine its use before we look at the uses themselves.

(1) Properties. — Agar is now known to consist of two fractions, agarose (Figure 16), a nonionic polysaccharide, and agaropectin, an anionic polysaccharide. Agarose is a polymer consisting of alternating 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galactopyranose units. Agaropectin is more variable in composition, but basically has the agarose structure with ester sulfate groups on some of the sugar units. The anionic nature of agar is due to the sulfate-containing agaropectin component. Calcium, sodium, and magnesium are the principal cations present as counterions in native agar (Guiseley, 1968). Figure 16 shows part of the molecule generally considered to incorporate the gelling function of agar.

The properties of an agar are governed both by the raw material from which it is made and by the care used in making it. Usually, the better agars--that is, those that are the

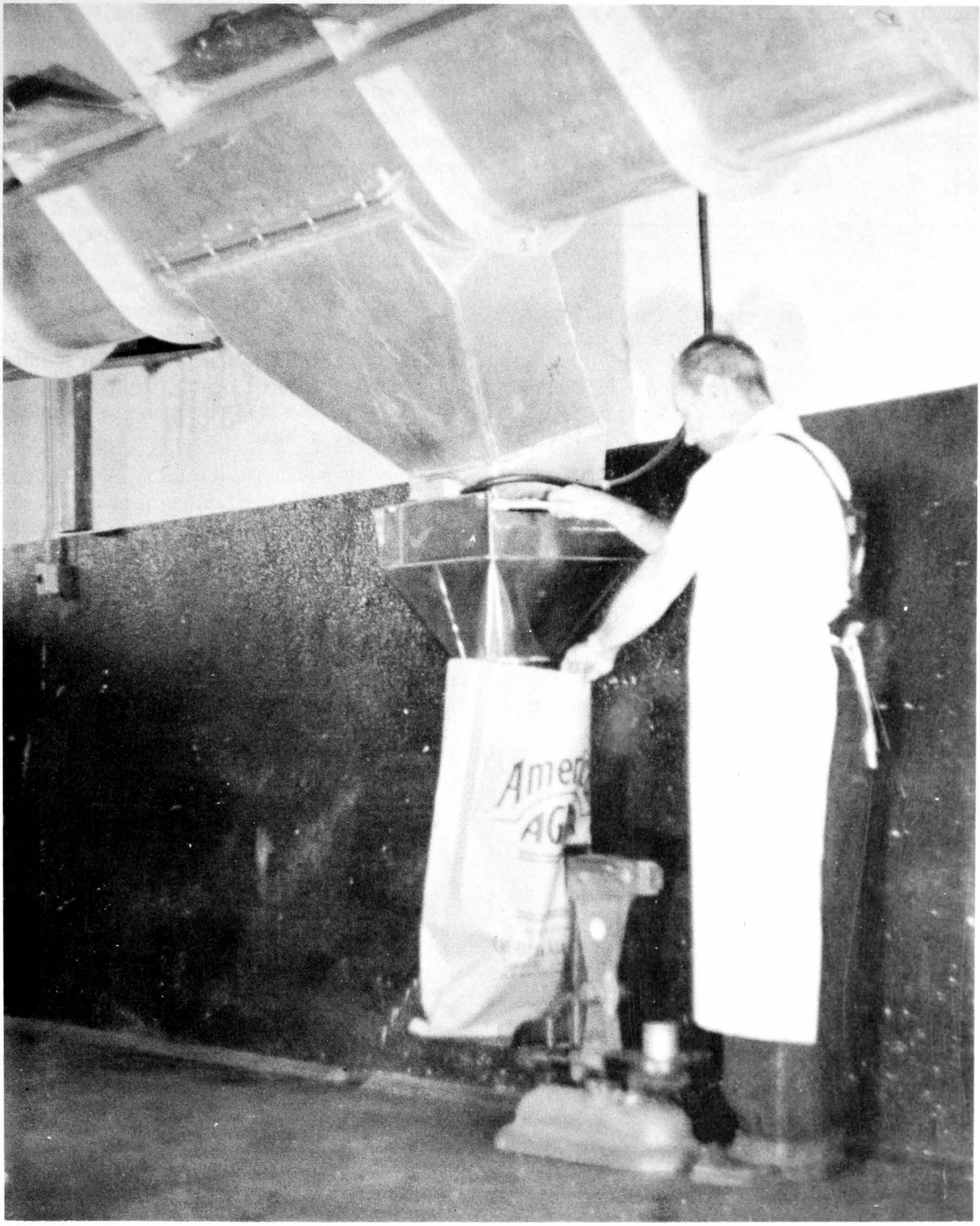

Figure 15.—Agar being packaged.

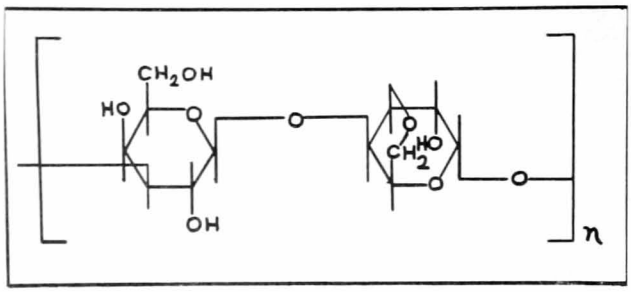

Figure 16.—Gelling component in agar molecule.

most carefully prepared--have the best color, the greatest freedom from extraneous materials, and the strongest gelling capability attainable from the raw material used. The most common variations in agar are in sol viscosity, gelling temperature, gelling strength, degree of syneresis, and gel clarity.

A relatively high temperature (95° to 100° C.) is required for agar to dissolve. The resulting sol has a low viscosity, which changes very slowly with changes in temperature. The transition from sol to gel, however, is fairly abrupt; it starts in the temperature range between 38° and 42° C. and is relatively unaffected by hydrocolloid concentration or other solutes. The gels that can be formed at concentrations of as low as 0.5 percent (the usual concentration is in the range of 1 to 2 percent) are "short"--that is, although they do not flow readily and tend to cut off quickly when poured, they are not stringy--and are thermally reversible. The transparency of the gels is moderately good, but variable.

(2) Primary uses. — The uses of agar are manifold (American Agar and Chemical Company, San Diego; Guiseley, 1968; Tressler and Lemon, 1951; Whistler and BeMiller, 1959), but its most important use is in bacteriological and fungal culture work. It is used in practically all bacteriological studies (Figure 17) of foods, water, drugs, and diseases. Antibiotics and vaccines are produced with the aid of agar.

Agar is unrivaled as a solidifying agent for culture media. Its outstanding properties are: (1) a firm, rubbery surface that is not easily ruptured when organisms are streaked across it by a needle; (2) the ability to remain liquid when cooled to 40° C., so that organisms may be thoroughly mixed with it at a temperature (usually 45° C.) that does not harm them; and (3) reversibility, which enables the agar to be alternately warmed into a sol or cooled

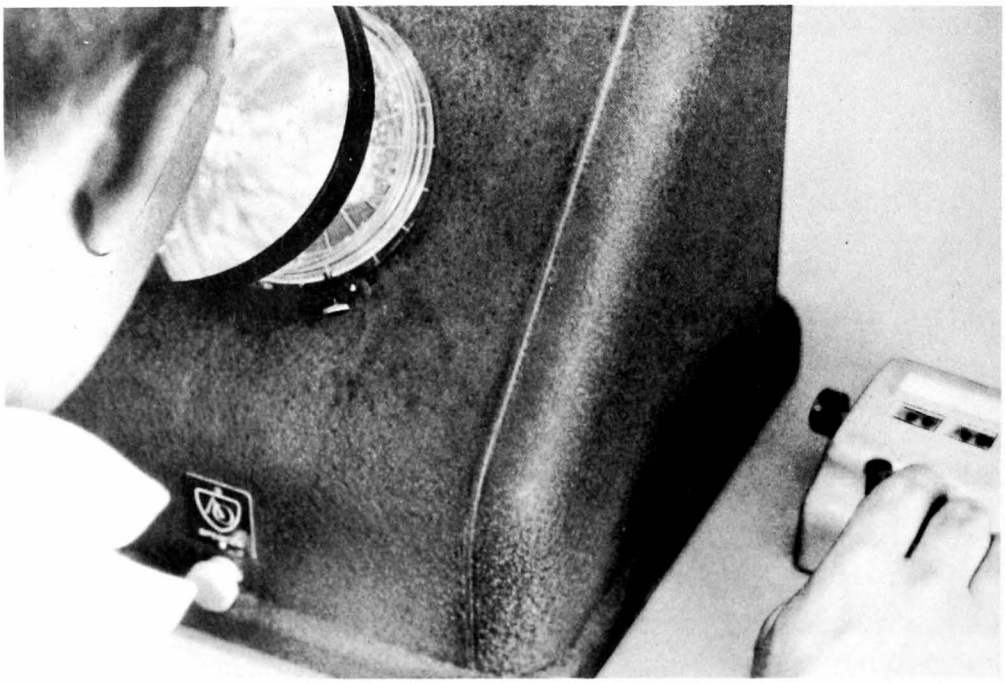

Figure 17.—Microbiologist counting colonies of microbes growing on agar used as a solidifying agent for culture media.

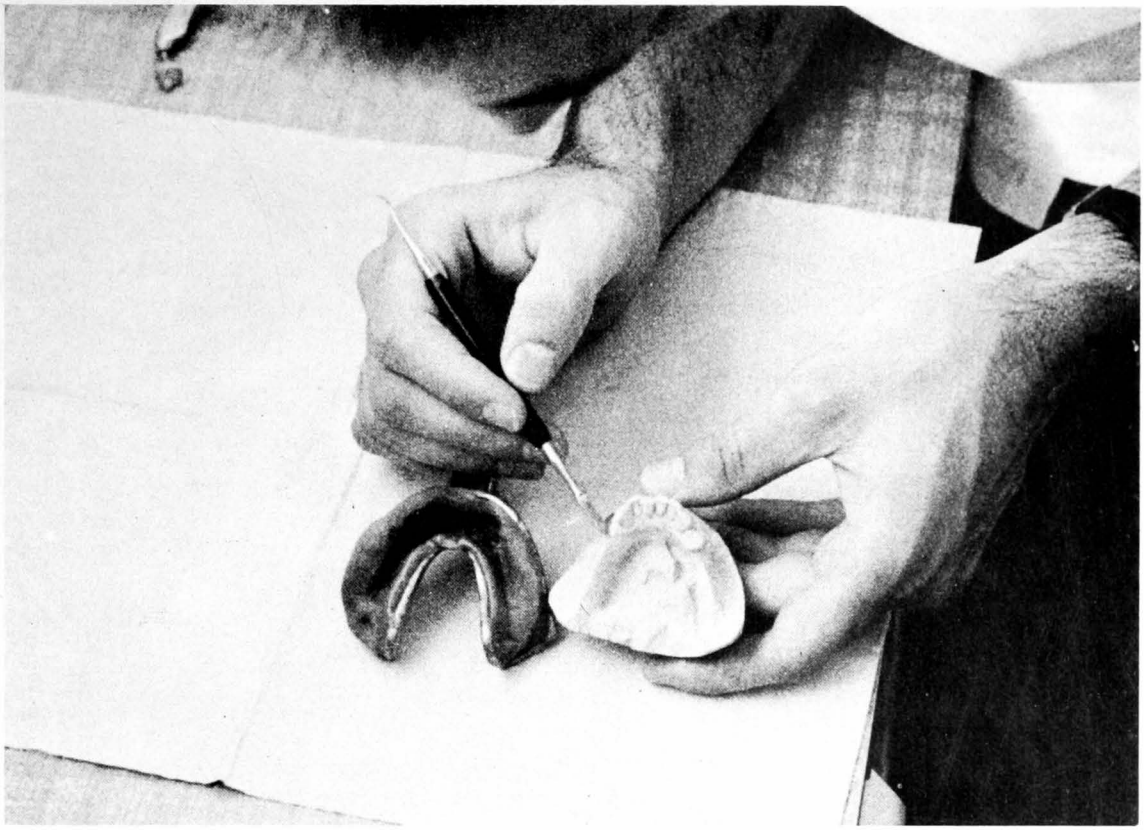

Figure 18.—Use of an agar compound in dental laboratories as an impression material for teeth.

into a gel. Even a dilute solution added to a nutrient material causes the material to set to a firm gel on which bacteria or fungi can grow. The gel will remain firm at 37° C., which is the temperature commonly used for incubating bacterial and fungal cultures. Another value of agar as a bacterial culture is its resistance to liquification. Bacteriological agar remains liquid when cooled to about 40° C., hence most organisms can be thoroughly distributed within it at a temperature that will not harm them. Many bacteria convert solid media such as gelatin into a liquid solution. Although some bacteria are capable of liquefying agar gel, there are relatively few of them.

In addition to its use as a culture for microorganisms, agar is used for food (both "as is" and as a medicine), in industrial processing operations, as a constituent of medical pills and capsules, and in pharmaceutical and cosmetic creams and jellies. In a number of countries, the transport of preserved cooked fish is aided by agar gel--imbedding the fish in the gel protects them from breaking up. It also prevents the constituents of certain fish, such as herring, from blackening the contents of the can.

It is used as a glue, for making silk and paper transparent, as a substitute for such products as gelatin and isinglass, for sizing silks and paper, for dying fabrics, in adhesives, in fish and potato bouillon, for clarifying liquids, for making beer wort, and as a lubricant in wire drawing.

Its other uses are widespread. Agar can be used to make jellies, salad dressing, icings, confections, and aspics that set at room temperature. Some physicians think that it is the only perfect laxative. Orchid culture would be much more difficult without it. People who, for medical or religious reasons, require edible emulsions and gels that are low in sugars, proteins, or animal derivatives find agar admixtures ideal. Agar may be used in dental laboratories in elastic impression material (Figure 18). Plastic surgeons and criminologists use it for making casts and impressions.

Figure 19.—Agar is used in the production of pharmaceuticals and cosmetics.

As a thickener, emulsifier, gelation agent, absorbent, lubricant, and inert carrier, it has many uses, as in the production of pharmaceuticals and wines (Figures 19 and 20).

2. Algin

Following the pattern established in our discussion of agar-agar, we first take up the production of algin and then its use.

a. Production.

(1) Harvesting.—Most of the algin produced in the United States is extracted from the giant kelp *Macrocystis pyrifera,* which is harvested in the offshore waters of the Eastern Pacific. It may also be extracted from *Laminaria digitata* and *Laminaria saccharina,* which grow along the North Atlantic Coast. The giant kelp is found in beds that vary from 50 feet to 1 mile wide and that are often several

miles long (Figure 21). It grows in areas where the water is from 25 to 80 feet deep, the bottom is rocky, and the ocean currents are strong. The rocky bottom, to which it clings, serves as a base for its rootlike structure, called a holdfast. The strong currents supply the constantly renewed nutrients necessary to sustain its growth.

On the Pacific Coast, the giant kelp is harvested with special harvesting vessels equipped with mechanical cutting and loading apparatus (Figure 22). The plants are cut about 3 feet below the surface of the water; cutting the surface growth permits greater penetration of sunlight and thereby promotes denser and more vigorous growth of the younger plants below. New shoots soon reach the surface, permitting the area to be harvested again in about 4 months (Chapman, 1952; Kelco Co., 1968; Newton, 1951; Whistler and BeMiller, 1959).

Figure 20.—Wine is one of the many products in which agar is used during manufacture.

Figure 21.—The giant kelp *(Macrocystis pyrifera)* forms interesting patterns on the surface of the ocean.

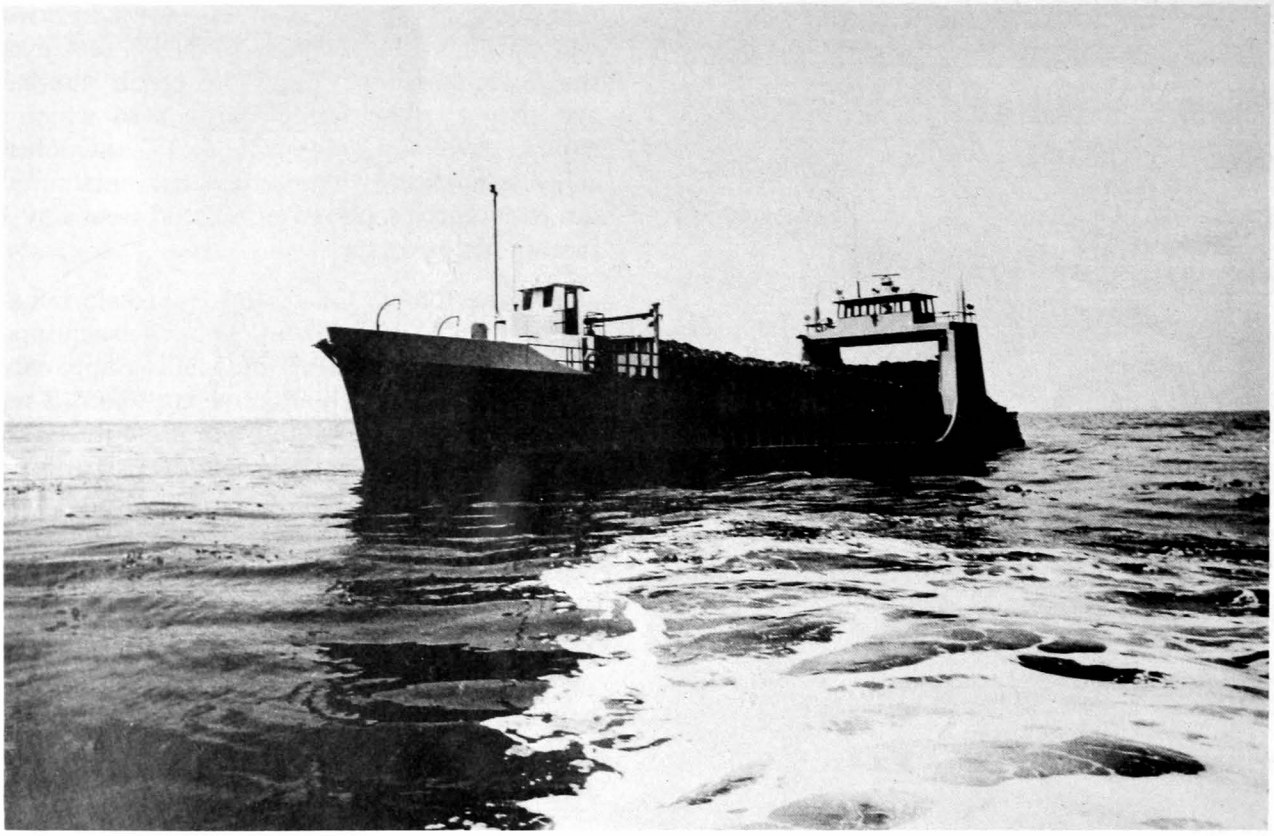

Figure 22.—Specially designed sea-going harvesters are used to cut and load kelp.

Since *Laminaria* species are less easily gathered, various handpicking methods are used. Grappling hooks hauled from a power boat at a depth of 12 to 15 feet are the usual harvesting instruments.

(2) Manufacturing. — Two processes primarily are used in the United States for the commercial production (Figure 23) of alginic acid and alginates (Chapman, 1952; Guiseley, 1968; Stoloff, 1954; Tressler and Lemon, 1957). Green's cold process is used on the Pacific Coast to extract the giant kelp, and the Le Gloahec-Herter process was formerly used on the Atlantic Coast to extract the *Laminaria* species. Alginates are no longer produced on the Atlantic Coast of the United States.

(*a*) *Green's process.*—In the cold process (Figure 24), fresh kelp is first leached for several hours with a weak solution of hydrochloric acid to reduce the content of salt. After being chopped and shredded, the leached kelp is digested with a soda-ash solution (40 to 50 pounds per ton of fresh kelp) at a pH of about 10 for about 30 minutes. The digestion process is then repeated. The product is next disintegrated in a hammer mill. Six volumes of water are added, and the mixture is maintained at a pH of 10.6 to 11.0. This mixture is pumped into a tank, where clarifying agents are added, and is allowed to settle. A diatomaceous-earth filter aid is mixed with the supernatant liquor, which is then filtered through a plate-and-frame filter press.

The filtrate, which contains the sodium alginate in solution, is treated with a 10-percent calcium chloride solution to precipitate the alginic acid as the calcium salt. The insoluble calcium alginate rises to the top, and the lower layers of the solution containing soluble salts and soluble organic matter are drained out and discarded. The curdlike calcium alginate is washed with fresh water and is bleached with a dilute solution of sodium hypochlorite.

After being drained, the calcium alginate is converted to alginic acid by treatment with 5-percent hydrochloric acid. The resulting

soluble calcium chloride and the excess acid are drained off through a screen. The remaining solid alginic acid is washed several times with acidulated water to remove any remaining calcium.

The purified alginic acid can be converted into stable sodium alginate or other alginate by treatment with the appropriate carbonate, oxide, or hydroxide.

(*b*) *Le Gloahec-Herter process.* — The Le Gloahec-Herter process (Figure 25) differs from Green's process in a number of ways. Its use of dilute calcium chloride for leaching enables it to remove laminaran and mannitol from the mass without adversely affecting the algin. The seaweed, after being leached, is washed with softened water and then is digested at a temperature of 140° F. in an alkaline medium. The digestion mass is heated and mixed, and the process continues until a homogeneous paste is obtained. The paste is diluted and beaten again, and air is introduced through fine apertures. The use of this latter process results in a product of high viscosity.

b. Use.

(1) Properties.—Algin is the general term designating the hydrophilic or water-loving derivatives of alginic acid (Guiseley, 1968; Kelco Co., 1968; Muncaster and Messina, 1961; Steiner and McNeely, 1951, 1954; Young and McLachlan, 1966). This natural colloid is a polyuronic acid composed mainly of β-(1-4)

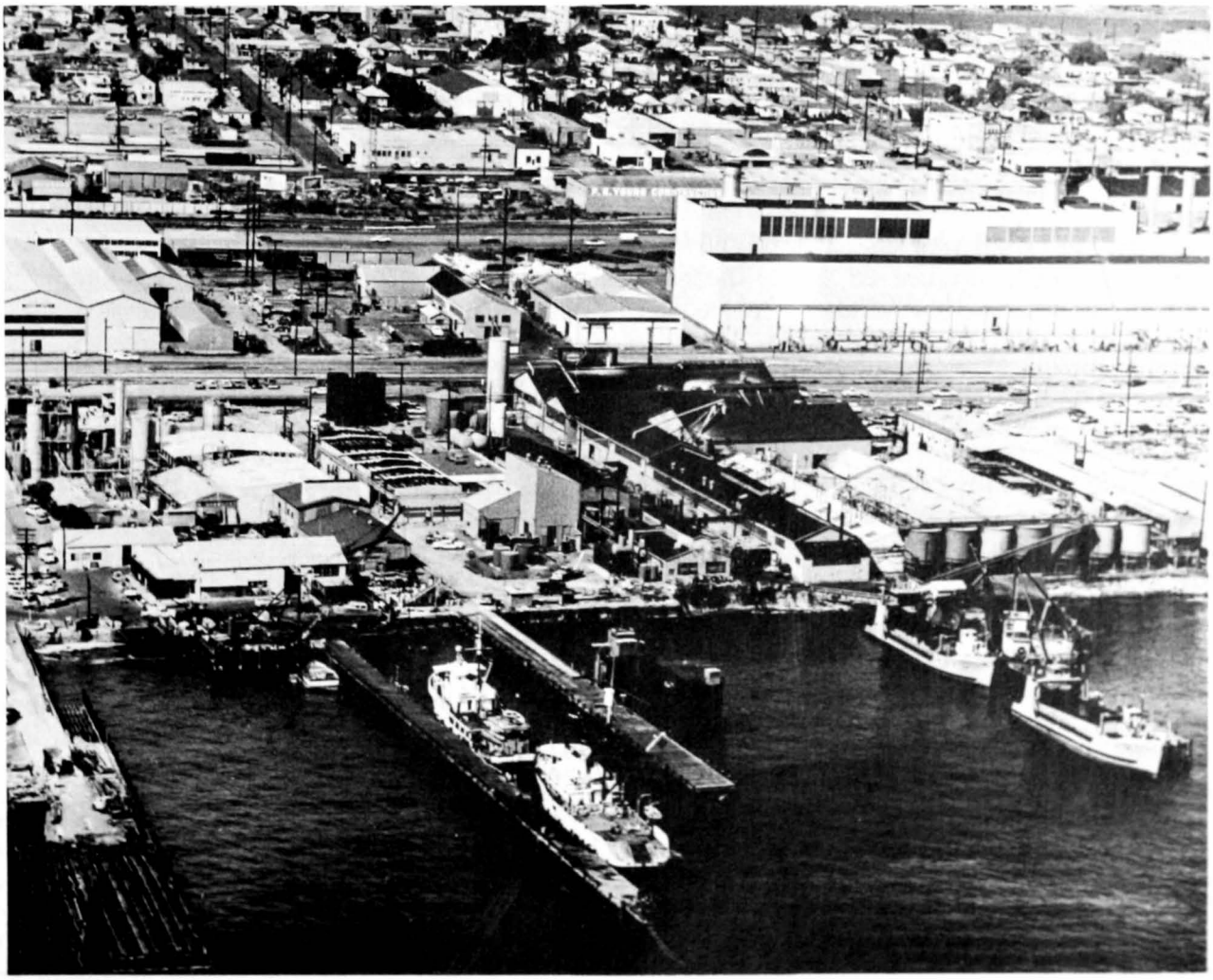

Figure 23.—Modern west coast plant for processing kelp into many useful products.

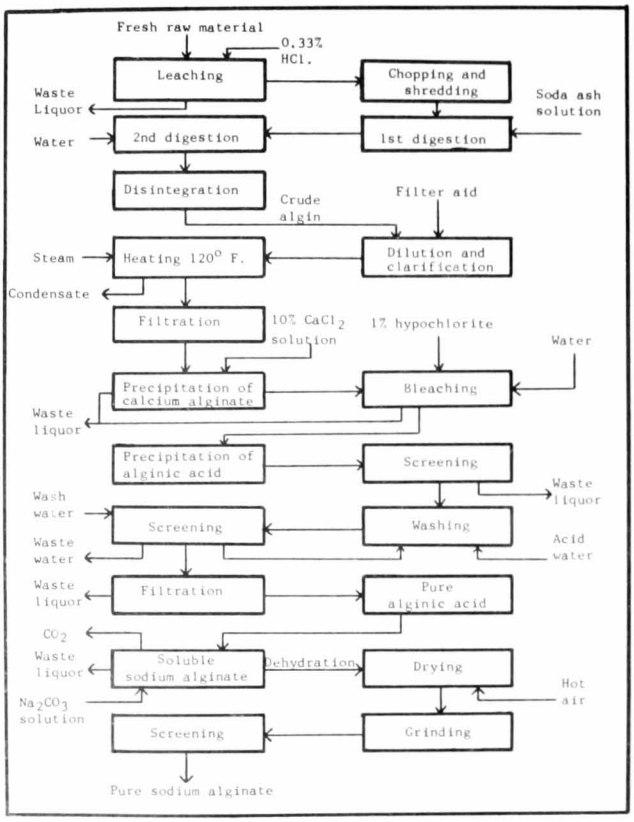

Figure 24.–Flow sheet of Green's cold process.

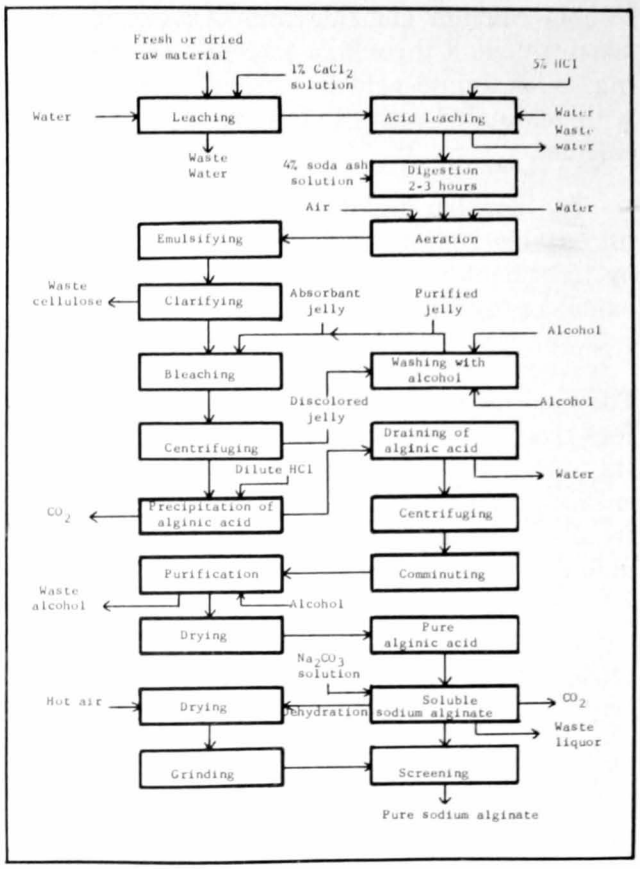

Figure 25.–Flow sheet of Le Gloahec-Herter process.

linked anhydro D-mannuronic acid and anhydro L-guluronic acid. Figure 26 shows the generally accepted structure of alginic acid.

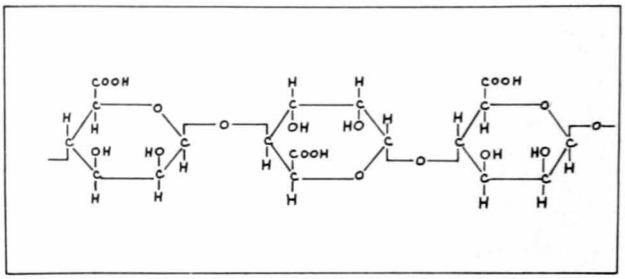

Figure 26.–Structure of alginic acid.

Most alginic acid is capable of absorbing 10 to 20 times its weight in water. When moist, it is readily soluble in dilute alkali, but when dried, it becomes hard and resistant to solvents. Careful control of their process enables manufacturers to supply products that can be used in numerous industrial and food applications.

The technical importance of alginic acid results principally from the properties of its salts. The alkali metal, ammonium salts, and magnesium salt dissolve readily in water and give solutions that do not coagulate or gel on being heated. Solutions of these salts are transparent, colorless, and essentially odorless. They have a wide range of controllable viscosity, which is affected by the addition of calcium ions to solutions of sodium alginate. Preparations may be thickened to creams or converted into jellies, depending on the amount of calcium salt added. Only a small concentration of algin is required. The calcium ions interact with the free carboxyl groups of the algin molecules, linking and intertwining them into a complex network that forms the gel structure.

The addition of about 10 to 25 percent of alkaline phosphates or carbonates, by weight of algin, improves the smoothness and the flow of algin solutions and decreases the viscosity. Such additions form a convenient method of raising the pH. Adding strong alkalis to an algin solution has no immediate effect below

a pH of about 12. At this pH, however, the solution will begin to thicken and form a gel.

Algin solutions can form films that are clear, tough, and flexible and that have good adherent qualities. Not only are these films resistant to greases, oils, fats, waxes, and organic solvents, but they also are compatible with the common hygroscopic plasticizers, such as glycerine and sorbitol. They can be made water resistant either by the addition of urea-formaldehyde-type resins, which make them insoluble on being heated, or by treatment with a solution of an alkaline-earth or heavy metal salt, such as zinc chloride or zirconium oxychloride. An additional method of making water-resistant films is to form a metallic derivative that is soluble in excess ammonium hydroxide. Drying the films drives off ammonia and makes the films insoluble. The metallic derivatives can be formed from the salts of zinc, aluminum, copper, chromium, or iron.

Some additional properties of the algin gel are:

1. No heating or cooling is required in the formation of the gel. Because gelation takes place readily at room temperature, the system is ideal for instant products. Gels can be formed hot or cold with milk or water.

2. The body of the gel can be specifically controlled for formulations ranging from quite light to very firm and heavy. The most effective way of changing the gel body to fit the requirements of a particular formulation, as we noted earlier, is to vary the concentrations of algin and calcium. Although the desired body can sometimes be attained by altering either concentration independently, maintaining a basic ratio of about 1 part calcium salt (by weight) to 3 parts algin (if the calcium salt is di- or tricalcium phosphate) is desirable.

3. Syneresis, or weeping, is greatly retarded because the algin molecule has a strong affinity for water and keeps it tightly bound within the system.

4. The gel has excellent stability toward heat even, for example, under the high temperatures required in the baking industry.

5. The sugar content or pH need not be adjusted for the gel to form. Because sugar and acid can be added only to satisfy flavor requirements, algin gel makes an excellent base for many dietetic products, such as instant milk shakes, puddings, and jellies.

(2) Primary uses.—Algin solutions have been used successfully (Chapman, 1952; Guiseley, 1968; Idson, 1956; Jackson, 1964; Kelco Co., 1968; Muncaster and Messina, 1961; Newton, 1951; Whistler and BeMiller, 1959) to stabilize emulsions and suspensions and to control the formation of crystals, particularly ice crystals. The uses of insoluble calcium alginate and alginic acid are based on their ability to absorb many times their own weight of water. They also can be formed into strong films or fibers, which can either be eaten or be converted back to soluble salts.

One of the most important uses of algin is as a stabilizer to give smooth body and texture to frozen desserts. Such a use is economical, because 1 pound of algin will stabilize about 150 gallons of ice cream.

Important new applications for algin in the food field have been developed during the past few years as a result of the availability of propylene glycol alginate (Figure 27). Although sodium alginate is precipitated as alginic acid at the low pH characteristic of French dressing, propylene glycol alginate is soluble. By acting both as a thickener and as

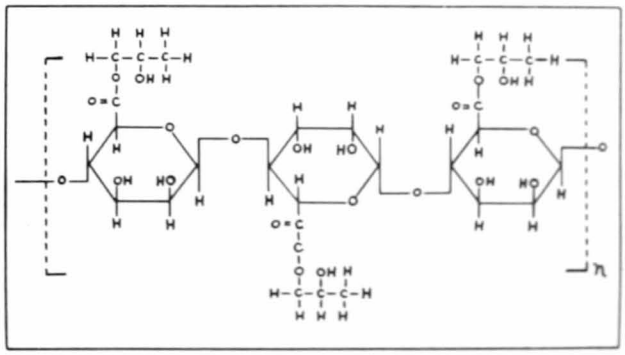

Figure 27.—Propylene glycol alginate.

an emulsifier, propylene glycol alginate prevents the oil in an oil-water emulsion from surfacing during many months of shelf life (Figure 28). It is also useful in acidic solutions, and thus stabilizes various sauces, syrups, and sherbets. It also functions as a very efficient beer-foam stabilizer at a level of about 1.5 pounds per 100 barrels of beer (Figure 29).

Sodium alginate can act as a stabilizing agent in cream substitutes, chocolate milk suspensions, marshmallows, and various drinks. It is a thickening agent for jams and sauces, food jellies, and custard (Figure 30). Various combinations of calcium alginate and water-soluble salts of alginic acid are used in icings and glazes. In the icings on cakes and sweet rolls, for example, the water-holding properties of algin prevent the icings from sticking to the wrappers or from disappearing into the cakes or rolls.

Many people in widely diversified food industries are working on products that are based on the algin gel system. Formulations are now being tested that will undoubtedly lead to many new products.

The algin products--sodium alginate, ammonium alginate, potassium alginate, and calcium

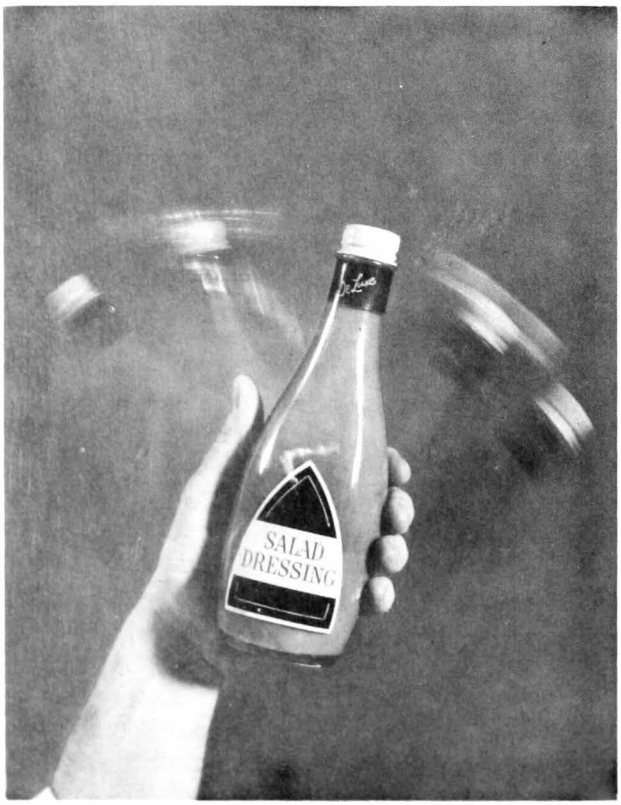

Figure 28.—Propylene glycol alginate is very useful as a stabilizer for salad dressing.

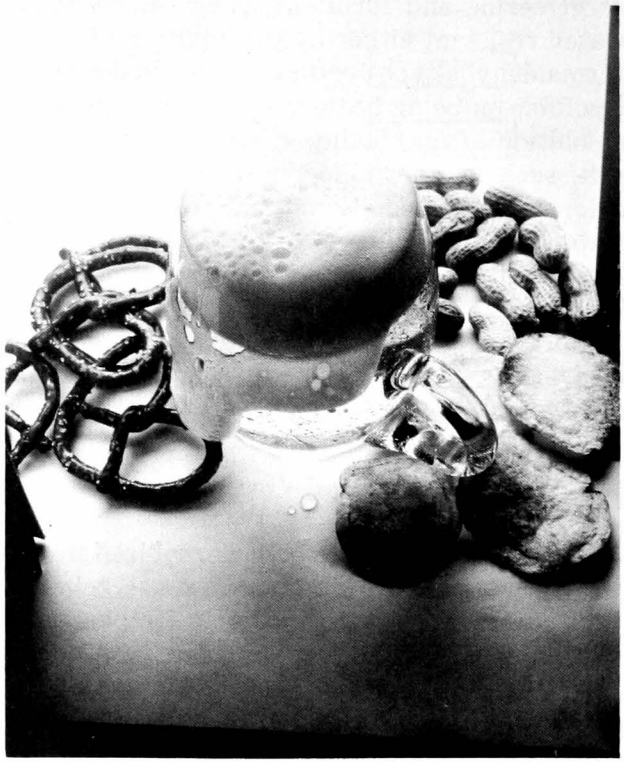

Figure 29.—Propylene glycol alginate delays the collapse of foam in beer.

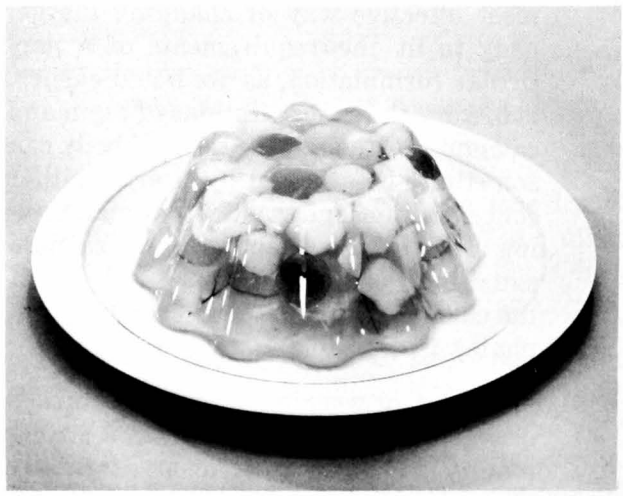

Figure 30.—Alginates are used as thickening agents in various food items.

alginate--are included in the list of substances judged by the U.S. Food and Drug Administration to be safe within the meaning of the Food Additives Amendment of 1958. Propylene glycol alginate is legally qualified under the Amendment for unrestricted use as a stabilizer, emulsifier, or thickener in all nonstandardized foods and confectionery products. Both sodium alginate and propylene glycol alginate are approved in a number of food standards promulgated by the Food and Drug Administration.

Jelly bases frequently serve as carriers for antiseptics and other drugs that are used for topical application (Figure 31). Algin jellies have emollient qualities that combat chafing, chapping, and ichiness, and that aid in the healing of burns. They yield nongreasy products that have no masking properties. They facilitate both application and removal; they are more stable than oil-based preparations.

Other pharmaceutical uses of algin include those for tablet disintegration and binding (Figure 31), for emulsifying mineral and vegetable oils, and for viscosity control of solutions and syrups; those in surgical jellies and in bulk laxatives; and those in suspending agents, shampoo foam-stabilizers, dental-impression compounds, and bodying agents for weight-control drinks and puddings.

Algin products are widely used in industry for emulsifying, thickening, suspending, stabilizing, gelling, plasticizing, flocculating, binding, and film forming. Plaster and cement products often contain algin products. This group of building materials includes wall-joint cements, texture paints, patching plasters, crack fillers, and acoustical plaster. Some of the advantages of algin-containing products are their improved ability to be worked (for example, their ability to be troweled), their tendency to restrict the penetration of moisture, their capacity to mix with and suspend pigments and clays, and their ability to prevent moisture from separating from the product on standing. These characteristics, because they result in increased working time during application, make the plaster or cement easier to handle and eliminate hairline cracks caused by rapid dehydration.

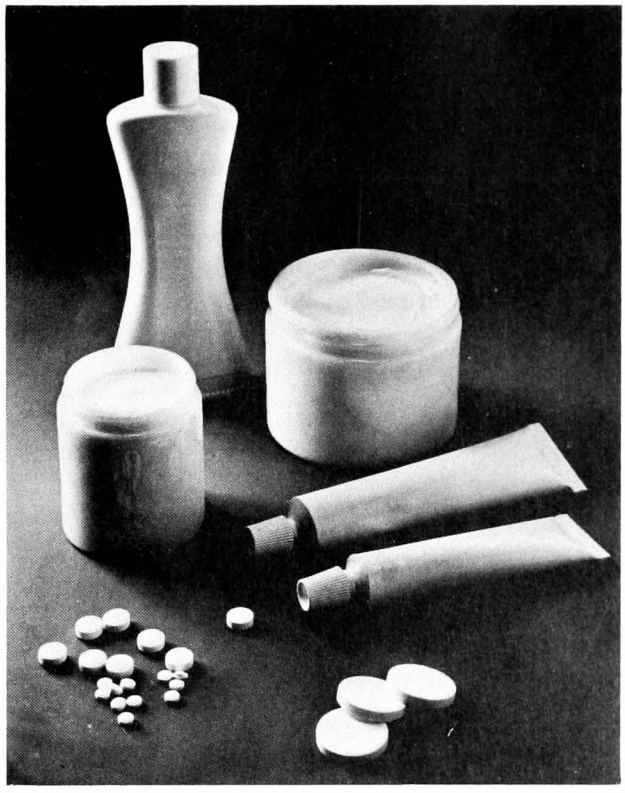

Figure 31.—The pharmaceutical and cosmetic industries have many uses for alginates.

Other industrial products containing algin include paints (Figure 32), ceramic glazes, welding rods, impression molds, products for

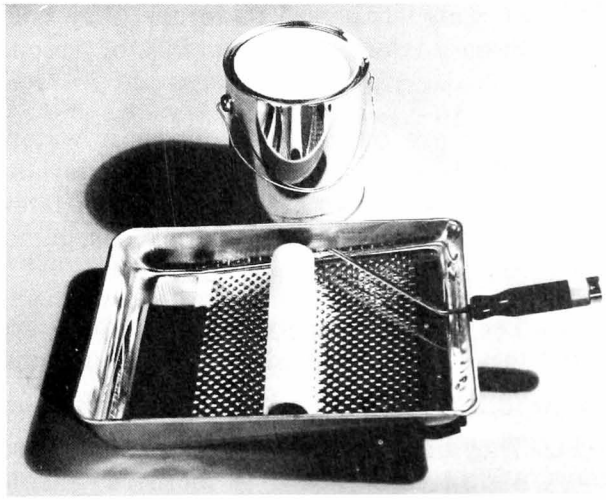

Figure 32.—Many paints and other industrial products contain alginates.

treating municipal and industrial water and boiler water, beet-sugar clarifiers, seed coatings, insecticides, and wax emulsions and polishes.

Sodium alginates are suitable for many textile applications. For example, in the printing of textile fabrics, algin is particularly effective as the thickening agent for dye solutions formulated into printing pastes. Often less than 2 percent of solids supply the necessary thickening to hold the printing characters of the dyes.

Although the largest share of algin used in textiles has been for printing, its use in sizing, finishing, rug backing, synthetic fiber manufacturing, and special new dying techniques is increasing.

Algin has several characteristics that make its products valuable ingredients to the paper and paperboard industry.

1. Being hydrophilic, they are readily soluble in either cold or warm water and are resistant to wax, grease, oils, and most organic solvents. They improve general printability and holdout of glossy ink.

2. They are excellent film formers for the production of continuous or semicontinuous films on the surface of paper or paperboard.

3. They control the penetration of water solutions. When used with other colloids or water-dispersed materials, they hold these products on the surface of fibrous webs.

4. They are compatible with most water-soluble and water-dispersible materials, such as starch, casein, resin and latex emulsions, protein, wax emulsions, gums, and plasticizers.

5. They are nontacky and therefore are ideal for high-speed calendar and sizing operations.

6. They improve gluing operations, because algin-treated board is more rewettable than are most other colloid-treated boards.

The alginate industry in the United States is highly oriented to research. Customer requirements form the basis for a continuous program of research and development of new products to meet industry needs. Researchers develop new formulas and prepare samples that are thoroughly tested, evaluated, and modified in the laboratory. Modern facilities are available for carrying out these research and development programs (Figure 33).

3. Carrageenan

a. Production.

(1) Harvesting.—Carrageenan is extracted primarily from the red seaweeds *Chondrus crispus* and *Gigartina stellata*. However, the name carrageenan also often applies to the extracts from other red seaweeds such as the *Eucheuma* and *Iridea* types, which are also used as sources of carrageenan in the United States. However, Irish moss (*Chondrus crispus*) (Figure 34) is the only native source of carrageenan in this country. It is harvested along the rocky shores of the North Atlantic Coast from New York to Nova Scotia (Chapman, 1952; Guiseley, 1968; Tressler and Lemon, 1951; Whistler and BeMiller, 1959).

North America imported some of its supplies from Europe until 1939, after which the industry for harvesting the plants and preparing the extract expanded in New England and the Maritime Provinces. Canada harvests large quantities of Irish moss and is now a competitor in world markets.

The Irish moss industry of New England represents the oldest seaweed industry in the United States; it dates from 1835. Harvesting began at Scituate, Massachusetts, which was considered to be the mossing center of the United States.

Irish moss grows from just above low-water level down to a depth of about 20 feet and can be gathered from May until about the first of September. Old fashioned methods of harvesting are still used. The mosslike algae are generally harvested by men working from dories with lead-weighted rakes that are 15 to 20 feet long (Figure 35). An experienced man

Figure 33.—Research and development programs for alginates are carried out in modern facilities.

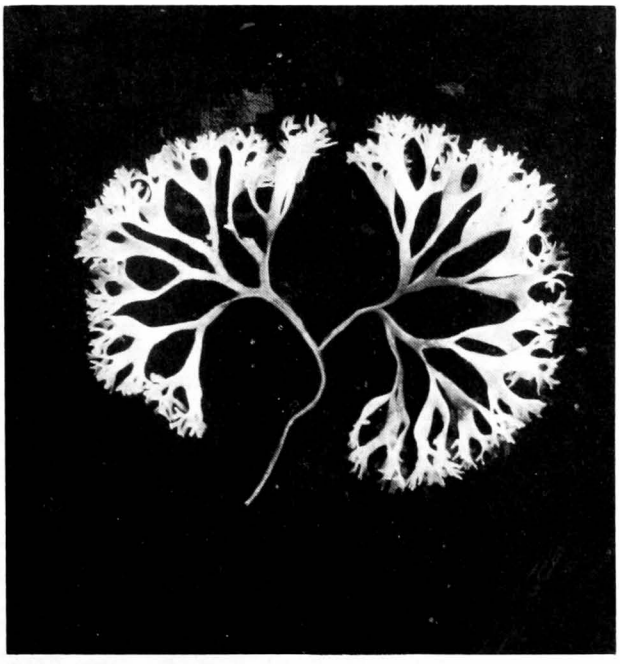

Figure 34.—Irish moss *(Chondrus crispus).*

can gather from 500 to 1,000 pounds per day under good harvesting conditions. In some areas, large amounts of Irish moss may be collected from beaches (Figure 36), where it is washed ashore during storms.

The plants, after being gathered, are either sun dried or dried in a mechanical dryer (Figure 37). Before the development of mechanical dryers, the moss was available as a sun-dried bleached or unbleached (black moss) raw material. Sun-bleached moss was prepared by washing in sea water periodically to prolong the drying process, thus allowing the sun's rays to destroy the pigments in the moss. This process usually required about 2 weeks. Irish moss can also be bleached artificially with sulfur dioxide. Residual sulfur dioxide, which is pale yellow, can be removed by washing the plant with a solution of potassium chloride. The industry has gradually been shifting to a

Figure 35.—Harvesting growing Irish moss (raking).

Figure 36.—Harvesting storm tossed seaweed on Prince Edward Island.

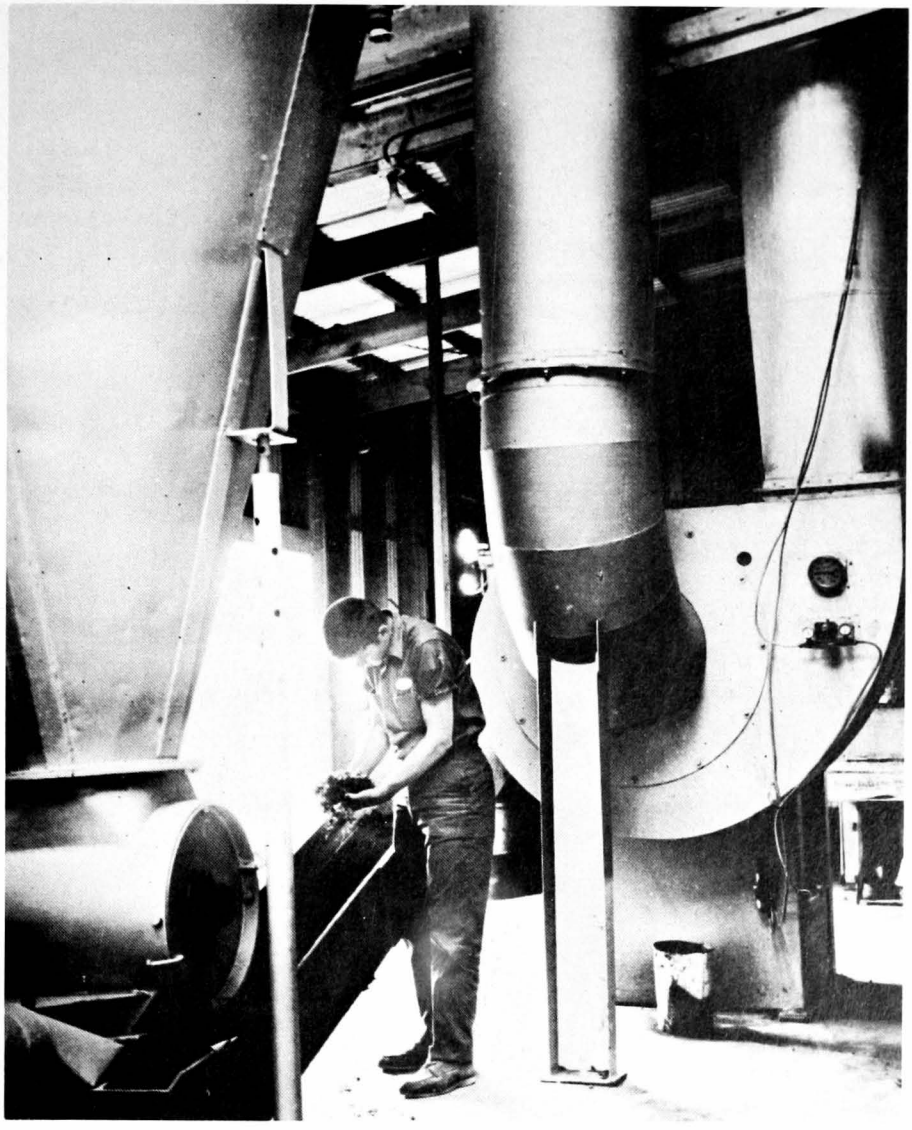

Figure 37.—A mechanical moss dryer.

greater use of unbleached moss in view of improved refining techniques and the installation of oil-fired dryers along the Northeast Coast of New England and the Maritime Provinces. These devices have greatly accelerated the drying operation.

Following the drying process, the moss is machine-baled for shipment to the processing plant (Figure 38) or storage in a seaweed warehouse (Figure 39).

(2) Manufacturing.—At the processing plant (Figures 40 and 41), water and mechanical devices give the moss a preliminary cleaning that serves to remove most of the extraneous substances such as salts, sand, stones, shells, and other undesirable materials. Then the cleaned material is extracted (Guiseley, 1968; Tressler and Lemon, 1951; Whistler and BeMiller, 1959) with hot water to which alkaline reagents such as calcium or sodium hydroxide are added. The extract is pumped into large tanks where it is held for several hours at 90° to 95° C., then, with the addition of a filter aid, the carrageenan solution is clarified by filtration in mechanical filter presses (Figure 42). The clarified extract may be concentrated prior to recovery of the extractive, either by drying on hot rolls or drums or by precipitating (through dehydration) with isopropyl alcohol. Prior to roll or drum drying (Figure 43), it may be necessary to decolorize the extract with charcoal to remove undesirable

Figure 38.—Moving baled moss.

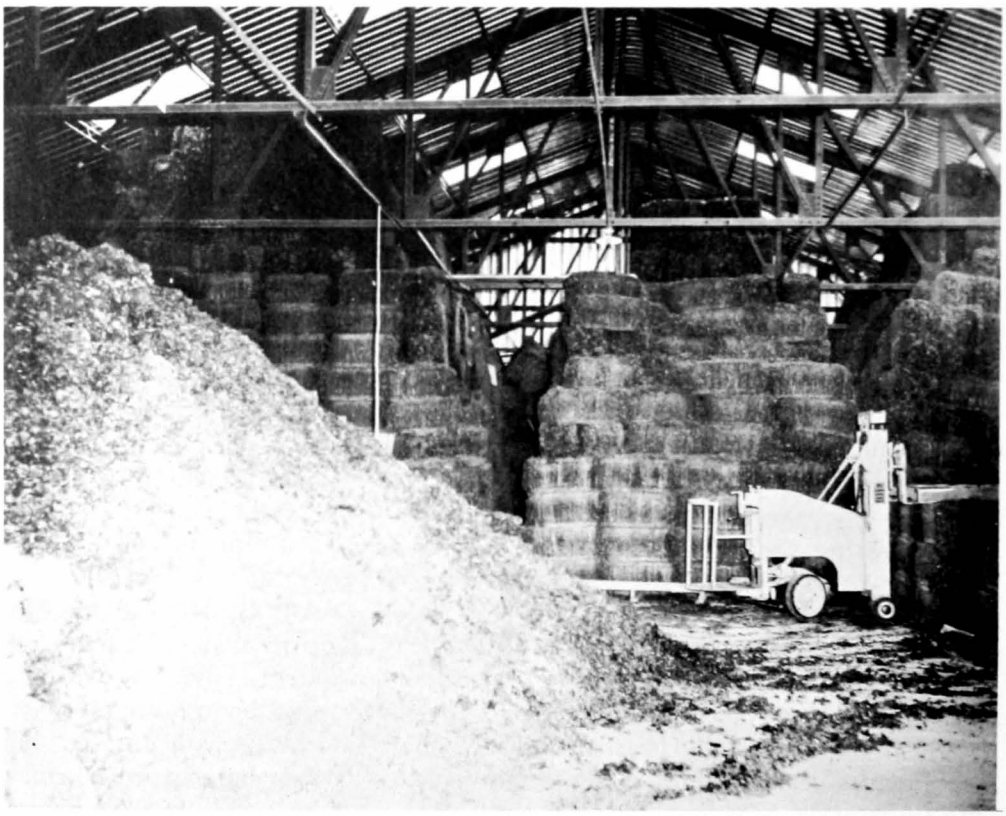

Figure 39.—View of a warehouse for seaweed, showing both loose and baled material.

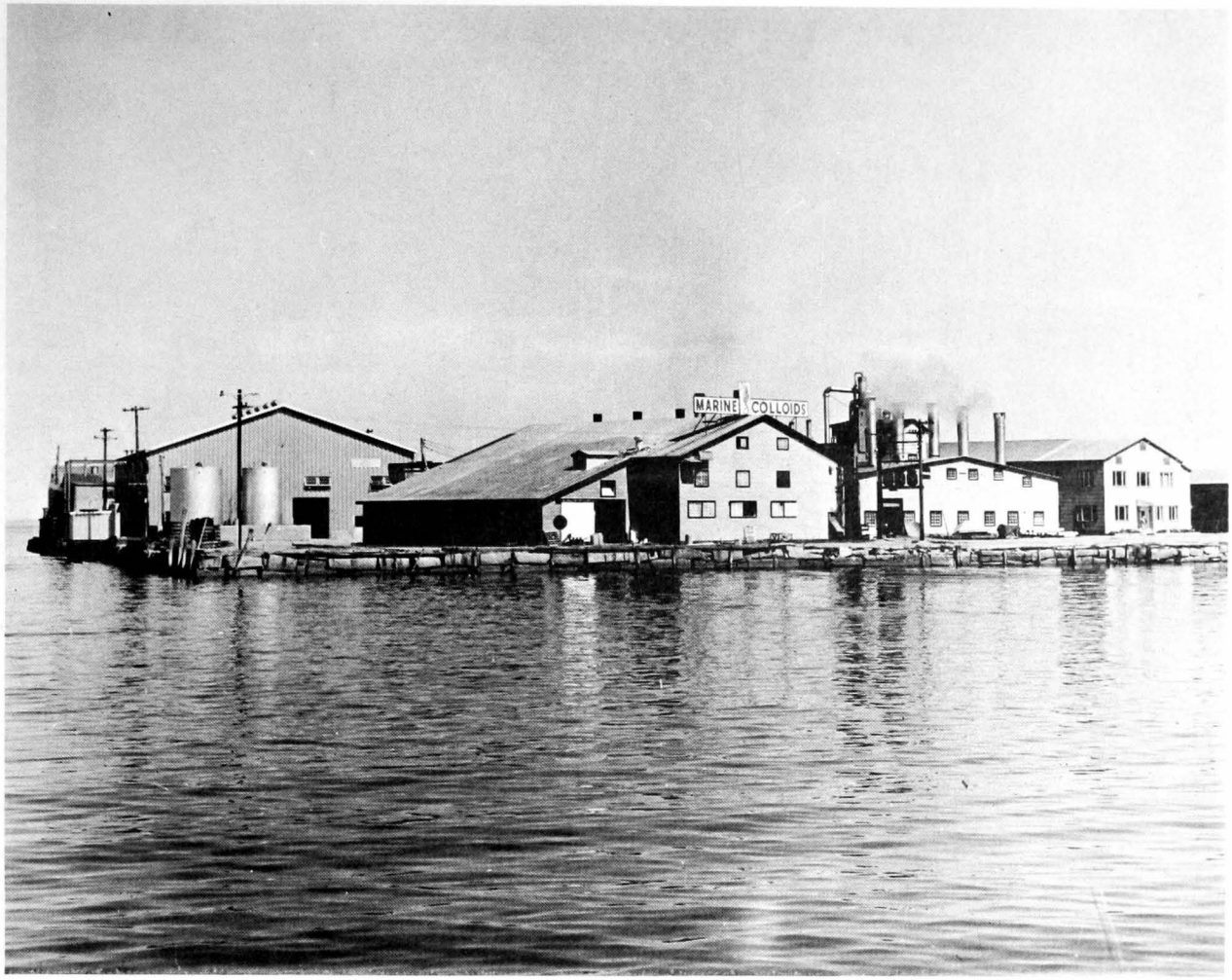

Figure 40.—A carrageenan producing plant in Maine.

pigments. If the extract is precipitated with isopropyl alcohol, further processing of the precipitate in rotary vacuum dryers is required to remove and recover the excess alcohol. Grinding, blending, and packaging (Figure 44) complete the process. Many refinements, some of which are trade secrets, have been added to the process; the results are a higher yield, a lighter color, more easily controlled viscosity, and better gel strength. A yield of 60 to 80 percent is commonly obtained from clean, thoroughly dried, raw material.

As with agar, the quantity and quality of Irish moss varies with location, weather, and water conditions. Achieving a prime end product, then, depends upon the selection of the raw material, the control of the processing, and the final blending of the production lots.

b. Use.

(1) Properties.—The hydrocolloid carrageenan is a galactosan sulfate having two fractions: kappa and lambda (de Virville and Feldman, 1964; Guiseley, 1968; Marine Colloids, Inc., 1966a, 1966b, 1967; Young and McLachlan, 1966). Kappa carrageenan is a polymer made up largely of alternating 1,3-linked β-D-galactopyranose-4-sulfate and 1,4-linked 3,6-anhydro-α-D-galactopyranose units. A minority of the latter units may be sulfated at C-2 or replaced by α-D-galactopyranose-2,6-disulfate units. Lambda carrageenan has a similar alternating structure, but the sugar units are respectively 1,3-linked, β-D-galactopyranose-2-sulfate and 1,4-linked α-D-galactopyranose-2,6-disulfate. Some of the 1,3-linked

Figure 41.—Aerial view of a carrageenan producing plant in Maine.

units may be unsulfated. Both the kappa and lambda fractions can be divided into two or more distinct subfractions. Figure 45 shows the structural relations.

A third major type of carrageenan, iota carrageenan, occurs mainly in the red seaweed *Eucheuma spinosum*. Iota carrageenan has recently been characterized as similar in structure to kappa carrageenan but with substantially all of the 3,6-anhydride sulfated at C-2.

The lambda fraction is viscous, nongelling, and insensitive to potassium; the kappa fraction is gelling and is sensitive to potassium.

Iota carrageenan gels with potassium and even more so with calcium. The calcium gels are more compliant than those with kappa carrageenan.

A carrageenan sol is a strongly charged polyelectrolyte in which the sulfates are about 60-percent ionized. One sulfate unit accompanies almost every hexose unit. Sols of carrageenan are very viscous at low concentration and form thermally reversible gels on the addition of certain compounds, particularly those of potassium, ammonium, and calcium.

The properties of a carrageenan solution are affected by the nature and relative amounts of other solutes such as sodium, calcium, and potassium contained in the solution. Theoretically, pure sodium kappa carrageenate and pure sodium lambda carrageenate solutions will not form a gel even if they are cooled to the freezing point. However, potassium kappa carrageenate will gel, as will calcium iota carrageenate.

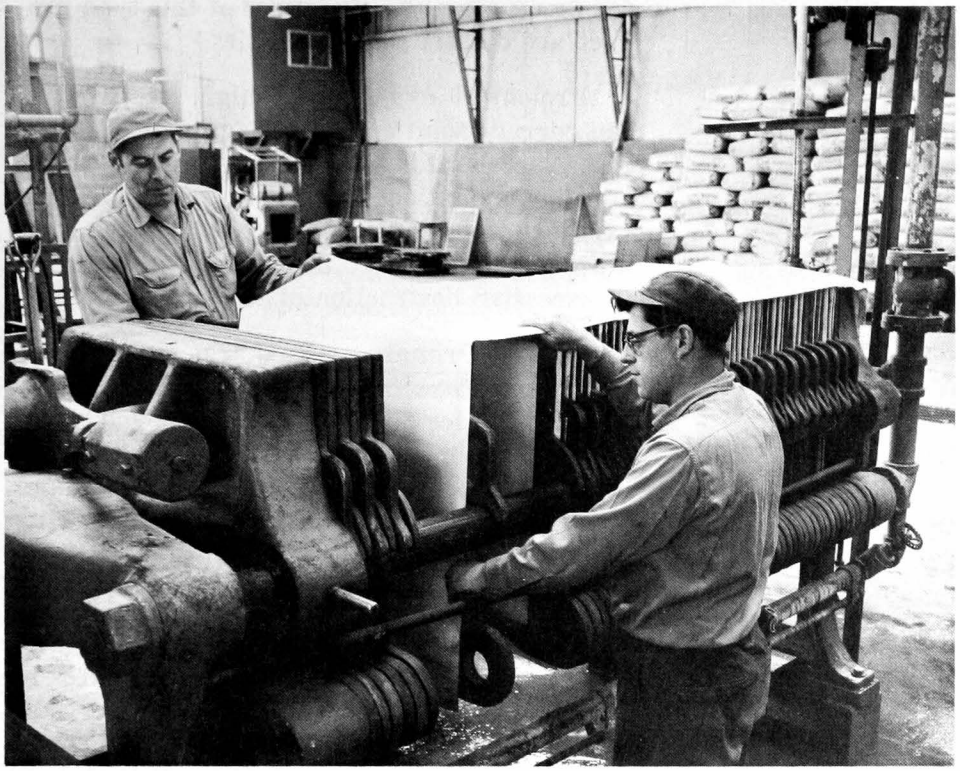

Figure 42.—Setting up a plate and frame filter press.

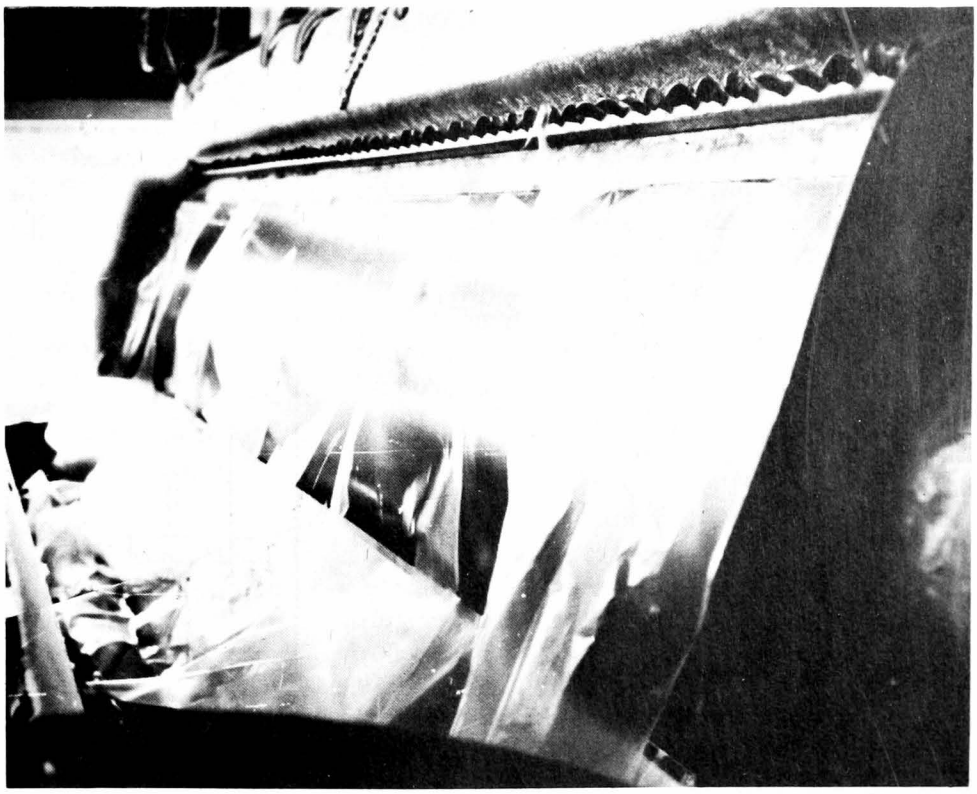

Figure 43.—Carrageenan coming off a steam-heated roll drier.

Figure 44.—The packaged carrageenan is shipped in fiber drums.

Because agar-agar and carrageenan do not have the same properties, they have different uses. Agar is best suited to uses in which the tendency to form a firm gel is required. Carrageenan is superior for uses that require high viscosity and the concomitant thickening, emulsifying, and suspending properties--although uses dependent upon its gel-forming properties are becoming increasingly important. Most notable are (1) its uses in milk systems wherein a broken gel structure is set up through interactions of (a) carrageenan and milk protein and (b) carrageenan and potassium ions from the milk or added cocoa; and (2) its uses in forming dessert gels. Extremely compliant --that is, gelatinlike--gels may be formed from combinations of various carrageenans or from combinations of carrageenan and locust bean gum. These gels have an advantage over gelatin gels in that they will set above room temperature and will not melt or become soft after being unmolded and placed on the dining table. Another advantage of carrageenan water gels is that they may be packed under high-temperature sterile conditions and stored for many months. Examples of this type product are dessert gels for babies.

Prolonged exposure to high temperature can degrade solutions of carrageenan. The effect is accelerated with decreasing pH and increasing oxidation potential. Below pH 6.0, exposure to high temperatures should be minimized; below pH 3.5, heating usually results in excessive destruction of the hydrocolloid.

(2) Primary uses.—Large quantities of carrageenan are used in nonsettling chocolate milk drinks, ice creams, sherbets, novelty ices, starch-based milk puddings, fruit pies, bakery and fountain specialties, oil emulsions, hand lotions, and toothpastes (Chapman, 1952; Guiseley, 1968; Københavns Pektinfabrik, 1963; Nilson and Wagner, 1959; Whistler and BeMiller, 1959).

When carrageenan is used in ice cream, its primary functions are to prevent ice crystal formation and to stabilize the milk protein system, thereby preventing whey separation.

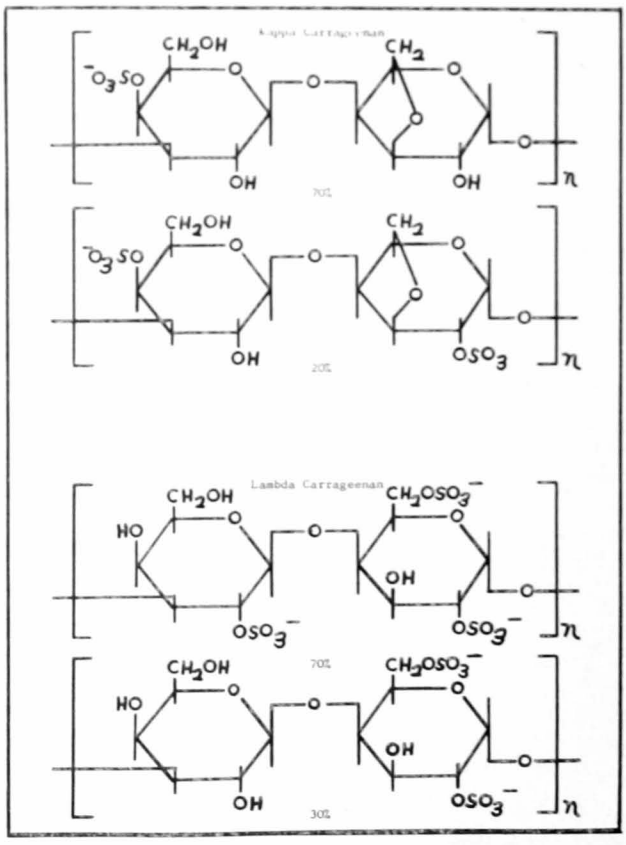

Figure 45.—Kappa and lamda carrageenan.

SUMMARY

Phycocolloids are colloids extracted from seaweeds. This article discusses these marine products, which are of considerable importance economically. They are considered in two groups--those of minor economic importance and those of major economic importance.

Phycocolloids of Minor Economic Importance

The phycocolloids of minor economic importance consist mainly of laminaran, funoran, and fucoidan. A variety of these phycocolloids have been used in the manufacture of surgical powders, textiles, and blood-clotting agents.

Phycocolloids of Major Economic Importance

The phycocolloids of major economic importance are agar-agar, algin, and carrageenan. Collectively, these phycocolloids are worth about 15 million dollars a year to the United States at the manufacturer's level.

Agar-agar.—The major problem in the production of agar-agar is the difficulty in getting the raw material. Agar is obtained primarily from *Gelidium cartilagineum,* a seaweed that is harvested by primitive methods, such as skindiving.

The seaweed is extracted in an autoclave, and the agar is purified in steps, one of which is freezing.

Agar consists of two fractions: agarose, a nonionic polysaccharide, and agaropectin, an anionic polysaccharide.

Agar has many uses as a thickener, emulsifier, gelation agent, absorbent, lubricant, and inert carrier. Its most important use is in the media for bacteriological cultures, for which it has ideal properties.

Algin.—Algin is obtained from the giant kelp *Macrocystis pyrifera,* which grows in beds that are from 50 feet to 1 mile wide and several miles long. This seaweed, which grows in the waters off Southern California and to the south, is gathered by means of special harvesting vessels equipped with mechanical cutting and loading equipment.

Green's cold process is used on the West Coast for processing *Macrocystis.*

Algin is a hydrophilic derivative of alginic acid. This natural colloid is a polyuronic acid composed of β-(1-4) linked anhydro D-mannuronic acid and anydro L-guluronic acid.

One of the most important uses of algin is as a stabilizer to give smooth body and texture to ice cream. In addition, it has hundreds of other uses in the food, pharmaceutical, cosmetic, and industrial fields.

Carrageenan.—The primary source of carrageenan is Irish moss (*Chondrus crispus*), which grows along the North Atlantic Coast. The mosslike alga is generally harvested by men working from dories and using lead-weighted rakes from 15 to 20 feet long.

Carrageenan is extracted from the Irish moss by hot water. The extractive is recovered from solution either by drying the solution on hot rolls or by precipitating it with isopropyl alcohol.

The hydrocolloid carrageenan is a galactosan sulfate having two fractions: kappa and lambda. Both kappa and lambda fractions can be divided into two or more distinct subfractions. A third major type of carrageenan, iota carrageenan, occurs mainly in the red seaweed *Eucheuma spinosum.*

Carrageenan is used primarily in nonsettling chocolate milk drinks and other foods as well as in various pharmaceuticals, such as hand lotions and toothpastes.

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Preliminary study of the proximate composition of fur seal, *Callorhinus ursinus*, meat. By Richard W. Nelson and Harold J. Barnett.	Seattle
Composition of Tennessee River fish and fishery products. By Richard A. Krzeczkowski.	Ann Arbor

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DIVISION OF EXPLORATORY FISHING

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Machine for separating northern shrimp, *Pandalus borealis*, from fish and trash in the catch. By Michael G. Corbett.	Gloucester
A tow bar system for seining farm ponds. By Kenneth L. Coon and James E. Ellis.	Ann Arbor

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by F. Bruce Sanford, Lena Baldwin, and Mary S. Fukuyama

A. APPROACH

Write your paper for a reader who has had advanced scientific training. Organize and write it in such a way that he can read it rapidly, yet understand it the first time through.

B. COMPONENTS OF THE PAPER

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Select a title that reveals the overall purpose of your research. When appropriate, include scientific names of species.

2. Abstract

Make the abstract semidescriptive: tell what the report is about, and end with a statement of your overall conclusion. (This conclusion will answer the question stated, or implied, by your overall purpose.) Keep the abstract short, but do not use the title of the paper as the assumed antecedent of otherwise irreferable pronouns.

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In the introduction, (1) orient the reader to your overall purpose, (2) state the purpose explicitly, (3) orient the reader to the subpurposes, and (4) end with a listing of the subpurposes.

Include in each orienting discussion all the important words that will occur in the subsequent statement of purpose. Avoid unnecessary reviews and economic data.

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Do not use such generalized divisions as "Experimental." Instead, be specific by making the main divisions of the paper correspond to the main divisions of your research—Experiment I, Experiment II, and so on. Give each experiment a specific title so that the reader will gain immediate insight into the scope of the experiment.

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a. Materials and methods.—Describe in detail the materials and the methods used in your first experiment. If the materials and methods used in succeeding experiments are similar to those in the first, merely describe the differences when you report the succeeding experiments.

If a method includes several closely consecutive steps, number them and write out the steps; use the active voice—for example, "In the separation of acids from the aqueous phase, the analyst:

1. Neutralized a 1-milliliter portion of the aqueous layer to a pH of 10 with 0.1 N NaOH.
2. Transferred the neutralized solution to Flask A.
3. Placed Flask A in a bath . . . ."

b. Results.—Report all numerical data in tables and graphs—avoid cluttering the text with numbers. In the discussion of results, do not repeat the data that are contained in the tables and graphs. Instead, analyze the data by pointing out significances and implications. Use summary tables; do not overwhelm the reader with unnecessary tables of raw data.

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Draw conclusions from your results. Make sure that the overall conclusion and the subconclusions correspond with your overall purpose and subpurposes. Present the conclusions in logical sequence.

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End the report with a summary. Make the summary quantitative, not merely descriptive. If the report is short, end it with "Summary and Conclusions." If it is long, separate the two.

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b. Graphs.—Number each graph. Place the title at the bottom of the graph, and end it with a period. In wording the title, follow the suggestions for titles of tables. Frame all 4 sides of the graph. Place tick marks on the inside of the frame at only the left and bottom sides unless you have compelling reason to do otherwise. Identify ordinate and abscissa; capitalize all letters in the identification. Place units of measurement in parentheses, and print them in lower case. Unless it clutters the graph, label each curve directly instead of using a legend or a key. Place each graph on a separate page. See the latest issue of *Fishery Industrial Research*.

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