⑫ **EUROPEAN PATENT APPLICATION**

�54 **Method for treating caustic refined glyceride oils for removal of soaps and phospholipids.**

�57 Adsorbents comprising amorphous silicas with effective average pore diameters of about 60 to about 5000 Angstroms are useful in processes for the removal of soaps and phospholipids (along with associated metal ions) from caustic treated or caustic refined glyceride oils.

CAPACITY OF SILICA FOR PL & SOAP
CAPACITY FOR PL&S VS PPM PL&S REMAINING IN OIL
"S=" IN LABEL DESIGNATES STARTING SOAP VALUE

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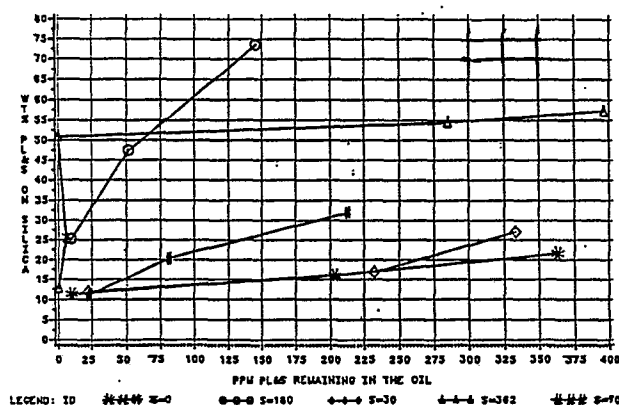
BACKGROUND OF THE INVENTION

This invention relates to a method for refining
glyceride oils by contacting the oils with an
adsorbent capable of removing certain impurities. More
specifically, it has been found that amorphous silicas
are quite effective in adsorbing both soaps and
phospholipids from caustic treated or caustic refined
glyceride oils, to produce oil products with substantially
lowered concentrations of these impurities. For purposes
of this specification, the term "impurities" refers to
soaps and phospholipids. The phospholipids are associated
with metal ions and together they will be referred to as
"trace contaminants." The term "glyceride oils" as used
herein is intended to encompass both vegetable and animal
oils. The term is primarily intended to describe the
so-called edible oils, i.e., oils derived from fruits or
seeds of plants and used chiefly in foodstuffs, but it is
understood that oils whose end use is as non-edibles are
to be included as well. The invention is applicable to
oils which have been subjected to caustic treatment, which
is the refining step in which soaps are formed in the oil.

Crude glyceride oils, particularly vegetable oils, are
refined by a multi-stage process, the first step of which
typically is "degumming" or "desliming" by treatment with
water or with a chemical such as phosphoric acid, citric
acid or acetic anhydrid. This treatment removes some but
not all gums and certain other contaminants. Some of the
phosphorus content of the oil is removed with the gums.
Either crude or degummed oil may be treated in a
chemical, or caustic, refining process. The addition of
an alkali solution, caustic soda for example, to a crude
or degummed oil causes neutralization of free fatty acids
to form soaps. This step in the refining process will be
referred to herein as "caustic treatment" and oils treated
in this manner will be referred to as "caustic treated
oils. Soaps generated during caustic treatment are an

impurity which must be removed from the oil because they have a detrimental effect on the flavor and stability of the finished oil. Moreover, the presence of soaps is harmful to the catalysts used in the oil hydrogenation

5   process.

Current industrial practice is to first remove soaps by centrifugal separation (referred to as "primary centrifugation"). In this specification, oils which have been subjected to caustic treatment and primary

10 centrifugation will be referred to as "caustic refined" oil. Conventionally, the caustic refined oil, which still has significant soap content, is subjected to a water wash, which dissolves the soaps from the oil phase into the aqueous phase. The two phases are separated by

15 centrifugation, although complete separation of the phases is not possible, even under the best of conditions. The light phase discharge is water-washed oil which now has reduced soap content. The heavy phase is a dilute soapy water solution. Frequently, the water wash and

20 centrifugation steps must be repeated in order to reduce the soap content of the oil below about 50 ppm. The water-washed oil then must be dried to remove residual moisture to below about 0.1 weight percent. The dried oil is then either transferred to the bleaching process or is

25 shipped or stored as once-refined oil.

A significant part of the waste discharge from the caustic refining of vegetable oil results from the water wash process used to remove soaps. In fact, a primary reason for refiners' use of the physical refining process

30 is to avoid the wastestream production associated with removal of soaps generated in the caustic refining process: since no caustic is used in physical refining, no soaps are generated. In addition, in the caustic refining process, some oil is lost in the water wash process. In

35 the caustic refining process to which this invention

relates, moreover, the dilute soapstock must be treated
before disposal, typically with an inorganic acid such as
sulfuric acid in a process termed acidulation. Sulfuric
acid is frequently used. It can be seen that quite a
5   number of separate unit operations make up the soap
removal process, each of which results in some degree of
oil loss. The removal and disposal of soaps and aqueous
soapstock is one of the most considerable problems
associated with the caustic refining of glyceride oils.
10   In addition to removal of soaps created in the
caustic refining process, phosphorus-containing trace
contaminants must be removed from the oil. The presence
of these trace contaminants can lend off colors, odors and
flavors to the finished oil product. These compounds are
15   phospholipids, with which are associated ionic forms of
the metals calcium, magnesium, iron and copper. For
purposes of this invention, references to the removal or
adsorption of phospholipids is intended also to refer to
removal or adsorption of the associated metal ions.
20   Adsorption of phosphorus on various adsorbents (for
example, bleaching earth) has been practiced but only with
respect to oils undergoing physical refining (in which no
soaps are generated) or in caustic refining subsequent to
water wash steps (in which the soaps are removed). No
25   adsorption process has accomplished the removal of both
soaps and phospholipids at an early stage of caustic
refining where large quantities of soaps are present.

SUMMARY OF THE INVENTION
30   A simple physical adsorption process has been found
whereby soaps and phospholipids can be removed from
caustic treated or caustic refined vegetable oils in a
single unit operation. This unique process completely
eliminates the need to subject caustic treated or caustic
35   refined oil to a water washing process in order to remove

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soaps. It also eliminates the need for a separate
adsorption process to reduce the phospholipid content of
the oil. The process described herein utilizes amorphous
silica adsorbents having an average pore diameter of

5   greater than 60A which can remove all or substantially all
soaps from the oil and which reduce the phospholipid
content on the oil to at least below 15 parts per million,
preferably below 5 parts per million, most preferably
substantially to zero.

10   It is the primary object of this invention to
introduce a single unit operation into the caustic
refining of glyceride oils which both eliminates soap and
reduces the phospholipid content of oils to acceptable
levels. Adsorption of soaps and phospholipids (together

15   with associated contaminants) onto amorphous silica in the
manner described offers tremendous advantage in caustic
refining by eliminating the several unit operations
required when conventional water-washing, centrifugation
and drying are employed to remove soaps from the oils. In

20   addition, this method eliminates the need for wastewater
treatment and disposal from those operations. Over and
above the cost savings realized from this tremendous
simplification of the oil processing, the overall value of
the product is increased since a significant by-product of

25   conventional caustic refining is dilute aqueous soapstock,
which is of very low value and requires substantial
treatment before disposal is permitted by environmental
authority.

It is also intended that use of the method of this
30   invention may reduce or potentially eliminate the need for
bleaching earth treatment. In this invention only one
adsorption step is used for removal of both soaps and
phospholipids. Additional treatment with bleaching earth
to remove these impurities typically will not be required.

Reduction or elimination of an additional bleaching earth step will result in substantial oil conservation as this step typically results in significant oil loss. Moreover, since spent bleaching earth has a tendency to undergo

5   spontaneous combustion, reduction or elimination of this step will yield an occupationally and environmentally safer process.

An additional object of the invention is to simplify the recovery costs and processing now associated with

10   preparation of the aqueous soapstock for use in the animal feed industry. The spent silica adsorbent can be used in animal feeds either as is or after acidulation to convert the soaps into free fatty acids. The need in the conventional caustic refining process for drying or

15   concentrating the dilute soapstock is eliminated by this invention.

DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graphic representation of adsorption isotherms for the capacity of amorphous silica for

20   combined phospholipids and soaps. The isotherms are based on the results of Example II as shown in Table V.

FIGURE 2 is a graphic representation of adsorption isotherms for the capacity of amorphous silica for phospholipids, for treated oil with $\leq$ 30 parts per million

25   residual soap. The isotherms are based on the results of Example II as shown in Table V.

DETAILED DESCRIPTION OF THE INVENTION

It has been found that amorphous silicas are particularly well suited for removing both soaps and

30   phospholipids from caustic refined glyceride oils. The process for the removal of these impurities, as described

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in detail herein, essentially comprises the steps of
selecting a caustic treated or caustic refined glyceride
oil which comprises soaps and phospholipids, selecting an
adsorbent which comprises a suitable amorphous silica,
5   contacting the caustic treated or caustic refined oil and
the adsorbent, allowing the soaps and phospholipids to be
adsorbed onto the amorphous silica, and separating the
adsorbent-treated oil from the adsorbent.

By the process of this invention soaps and
10   phospholipids can be removed from oils in a single
adsorption step. Moreover, it has been found that the
presence of increasing levels of soap in the oil to be
treated actually enhances the capacity of amorphous silica
to adsorb phosphorus. That is, the presence of soaps at
15   levels below the maximum adsorbent capacity of the silica
makes it possible to substantially reduce phosphorus
content at lower silica usage than required in the absence
of soaps.

The Oils

20   The process described herein can be used for the
removal of phospholipids from any caustic refined
glyceride oil, for example, oils of soybean, peanut,
rapeseed, corn, sunflower, palm, coconut, olive,
cottonseed, etc. The caustic refining process involves
25   the neutralization of the free fatty acid content of
crude or degummed oil by treatment with bases, such as
sodium hydroxide or sodium carbonate, which typically are
used in aqueous solution. The neutralized free fatty acid
present as the alkali or alkaline earth salt is defined as
30   soap. The soap content of caustic treated oil will vary
depending on the free fatty content of the unrefined oil.
Values disclosed as typical in the industry vary from
about 300 ppm soap for caustic treated oil (Erickson, Ed.,
Handbook of Soy Oil Processing and Utilization, Chapter 7,

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"Refining," p. 91 (1980)), to about 10-50 ppm soap for
caustic treated and primary centrifuged oil (Christenson,
Short Course, Processing and Quality Control of Fats and
Oils, Fig. 1, presented at Amer. Oil Chemists' Soc. (May
5   5-7, 1983). Fully refined oils must have soap values
approaching zero. Conventional separation and
water-washing processes remove about 90% of the soap
content generated by the caustic treatment step. The
process disclosed herein will reduce soaps to levels
10   acceptable to the industry, that is, less than about 10
ppm, preferably less than about 5 ppm, most preferably
about zero ppm, without the use of water wash steps.

Removal of trace contaminants (phospholipids and
associated metal ions) from edible oils also is a
15   significant step in the oil refining process because
they can cause off colors, odors and flavors in the
finished oil. Typically, the acceptable concentration of
phosphorus in the finished oil product should be less than
about 15.0 ppm, preferably less than about 5.0 ppm,
20   according to general industry practice. As an
illustration of the refining goals with respect to trace
contaminants, typical phosphorus levels in soybean oil at
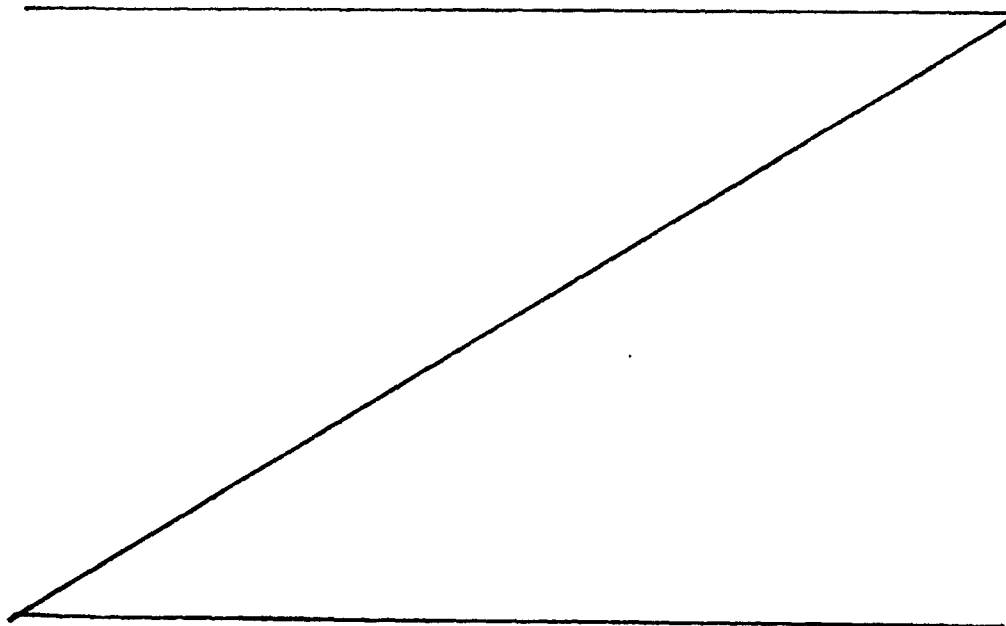various stages of chemical refining are shown in Table I.

TABLE I[1]

Stage	Trace Contaminant Levels (ppm)					
	P	Ca	Mg	Fe	Cu	Soaps (ppm)
Crude Oil	450-750	1-5	1-5	1-3	.03-.05	0
Degummed Oil	60-200	1-5	1-5	.4-.5	.02-.04	0
Caustic Treated Oil[2]	60-750	1-5	1-5	.4-.3	.02-.05	7500-12,500
Primary Centrifuged Oil	60-200	1-5	1-5	.4-.5	.02-.04	300
Caustic Refined Oil	10-15	1	1	0.3	.003	10-50
End Product	1-15	1	1	.1-.3	.003	0

1 - Data assembled from the Handbook of Soy Oil Processing and Utilization, Table I, p. 14, p.91, p.119, p.294 (1980), and from Fig. 1 from Christenson, Short Course: Processing and Quality Control of Fats and Oils, presented at American Oil Chemists' Society, Lake Geneva, WI (May 5-7, 1983).

2 - Either Crude Oil or Degummed Oil may be used to prepare Caustic Treated Oil.

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In addition to phospholipid removal, the process of
this invention also removes from edible oils ionic forms of
the metals calcium, magnesium, iron and copper, which are
believed to be chemically associated with phospholipids, and
5   which are removed in conjunction with the phospholipids.
These metal ions themselves have a deleterious effect on the
refined oil products. Calcium and magnesium ions can result
in the formation of precipitates, particularly with free
fatty acids, resulting in undesired soaps in the finished
10   oil. The presence of iron and copper ions promote oxidative
instability. Moreover, each of these metal ions is
associated with catalyst poisoning where the refined oil is
catalytically hydrogenated. Typical concentrations of these
metals in soybean oil at various stages of chemical refining
15   are shown in Table I. Throughout the description of this
invention, unless otherwise indicated, reference to the
removal of phospholipids is meant to encompass the removal
of associated metal ions as well.

The Adsorption Process - The amorphous silicas
20   described below exhibit very high capacity for adsorption of
soaps and phospholipids. The capacity of the silica for
phospholipids is improved with increasing soap levels in the
starting oil, provided that sufficient silica is used to
obtain adsorbent-treated oil with soap levels of
25   approximately 30 ppm or less. It is when the residual soap
levels (in the adsorbent-treated oil) fall below about
30 ppm that the increased capacity of the silica for
phospholipid adsorption is seen. It is believed that the
total available adsorption capacity of amorphous silica is
30   about 50 to 75 wt.% on a dry basis.
The silica usage should be adjusted so that the total
soap and phospholipid content of the caustic treated or
caustic refined oil does not exceed about 50 to 75 wt.% of
the silica added on a dry basis. The maximum adsorption

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capacity observed in a particular application is expected to be a function of the specific properties of the silica used, the oil type and stage of refinement, and processing conditions such as temperature, degree of mixing and

5   silica-oil contact time. Calculations for a specific application are well within the knowledge of a person of ordinary skill as guided by this specification.

The adsorption step itself is accomplished by conventional methods in which the amorphous silica and the

10   oil are contacted, preferably in a manner which facilitates the adsorption. The adsorption step may be by any convenient batch or continuous process. In any case, agitation or other mixing will enhance the adsorption efficiency of the silica.

15   The adsorption can be conducted at any convenient temperature at which the oil is a liquid. The caustic refined oil and amorphous silica are contacted as described above for a period sufficient to achieve the desired levels of soap and phospholipid in the treated oil. The specific

20   contact time will vary somewhat with the selected process, i.e., batch or continuous. In addition, the adsorbent usage, that is, the relative quantity of adsorbent brought into contact with the oil, will affect the amount of soaps and phospholipids removed. The adsorbent usage is

25   quantified as the weight percent of amorphous silica (on a dry weight basis after ignition at 1750°F), calculated on the basis of the weight of the oil processed. The preferred adsorbent usage is at least about 0.01 to about 1.0 wt.%, dry basis, most preferably at least about 0.1 to about 0.15

30   wt.%, dry basis.

As seen in the Examples, significant reduction in soap and phospholipid content is achieved by the method of this invention. The soap content and the phosphorus content of the treated oil will depend primarily on the oil itself, as

35   well as on the silica, usage, process, etc. For example, by

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reference to Table I, it will be appreciated that the
initial soap content will vary significantly depending
whether the oil is treated by this adsorption method
following caustic treatment or following primary
5   centrifugation. Similarly, the phosphorus content will be
somewhat reduced following degumming, caustic treatment
and/or primary centrifuge. However, phosphorus levels of
less than 15 ppm, preferably less than 5.0 ppm, and most
preferably less than 1.0 ppm, and soap levels of less than
10   50 ppm, preferably less than about 10 ppm and most
preferably substantially zero ppm, can be achieved by this
adsorption method.

Following adsorption, the soap and phospholipid
enriched silica is removed from the adsorbent-treated oil by
15   any convenient means, for example, by filtration or
centrifugation. The oil may be subjected to additional
finishing processes, such as steam refining, bleaching
and/or deodorizing. With low phosphorus and soap levels, it
may be feasible to use heat bleaching instead of a bleaching
20   earth step, which is associated with significant oil losses.
Even where bleaching earth operations are to be employed,
simultaneous or sequential treatment with amorphous silica
and bleaching earth provides an extremely efficient overall
process. By first using the method of this invention to
25   decrease the soap and phospholipid content, and then
treating with bleaching earth, the effectiveness of the
latter step is increased. Therefore, either the quantity of
bleaching earth required can be significantly reduced, or
the bleaching earth will operate more effectively per unit
30   weight. The spent silica may be used in animal feed, either
as is, or following acidulation to reconvert the soaps into
fatty acids. Alternatively, it may be feasible to elute the
adsorbed impurities from the spent silica in order to
re-cycle the silica for further oil treatment.

The Adsorbent

The term "amorphous silica" as used herein is intended to embrace silica gels, precipitated silicas, dialytic silicas and fumed silicas in their various prepared or

5   activated forms. Both silica gels and precipitated silicas are prepared by the destabilization of aqueous silicate solutions by acid neutralization. In the preparation of silica gel, a silica hydrogel is formed which then typically is washed to low salt content. The washed hydrogel may be

10   milled, or it may be dried, ultimately to the point where its structure no longer changes as a result of shrinkage. The dried, stable silica is termed a xerogel. In the preparation of precipitated silicas, the destabilization is carried out in the presence of polymerization inhibitors,

15   such as inorganic salts, which cause precipitation of hydrated silica. The precipitate typically is filtered, washed and dried. For preparation of gels or precipitates useful in this invention, it is preferred to initially dry the gel or precipitate to the desired water content.

20   Alternatively, they can be dried and then water can be added to reach the desired water content before use. Dialytic silica is prepared by precipitation of silica from a soluble silicate solution containing electrolyte salts (e.g., $NaNO_3$, Na_2SO_4, KNO_3) while electrodialyzing, as described in

25   pending U.S. patent application Serial No. 533,206 (Winyall), "Particulate Dialytic Silica," filed September 20, 1983. Fumed silicas (or pyrogenic silicas) are prepared from silicon tetrachloride by high-temperature hydrolysis, or other convenient methods. The specific manufacturing

30   process used to prepare the amorphous silica is not expected to affect its utility in this method.

In the preferred embodiment of this invention, the silica adsorbent will have the highest possible surface area in pores which are large enough to permit access to the soap

35   and phospholipid molecules, while being capable of

maintaining good structural integrity upon contact with the oil. The requirement of structural integrity is particularly important where the silica adsorbents are used in continuous flow systems, which are susceptible to

5   disruption and plugging. Amorphous silicas suitable for use in this process have surface areas of up to about 1200 square meters per gram, preferably between 100 and 1200 square meters per gram. It is preferred, as well, for as much as possible of the surface area to be contained in

10   pores with diameters greater than 60A.

     The method of this invention utilizes amorphous silicas with substantial porosity contained in pores having diameters greater than about 60A, as defined herein, after appropriate activation. Activation typically is

15   accomplished by heating to temperatures of about 450 to 700°F in vacuum. One convention which describes silicas is average pore diameter ("APD"), typically defined as that pore diameter at which 50% of the surface area or pore volume is contained in pores with diameters greater than the

20   stated APD and 50% is contained in pores with diameters less than the stated APD. Thus, in amorphous silicas suitable for use in the method of this invention, at least 50% of the pore volume will be in pores of at least 60A diameter. Silicas with a higher proportion of pores with diameters

25   greater than 60A will be preferred, as these will contain a greater number of potential adsorption sites. The practical upper APD limit is about 5000A.

     Silicas which have measured intraparticle APDs within the stated range will be suitable for use in this process.

30   Alternatively, the required porosity may be achieved by the creation of an artificial pore network of interparticle voids in the 60 to 5000A range. For example, non-porous silicas (i.e., fumed silica) can be used as aggregated particles. Silicas, with or without the required porosity,

35   may be used under conditions which create this artificial

pore network. Thus the criterion for selecting suitable
amorphous silicas for use in this process is the presence of
an "effective average pore diameter" greater than 60A. This
term includes both measured intraparticle APD and

5   interparticle APD, designating the pores created by
aggregation or packing of silica particles.

The APD value (in Angstroms) can be measured by several
methods or can be approximated by the following equation,
which assumes model pores of cylindrical geometry:

10   (1) $APD (A) = \dfrac{40,000 \times PV \; (cc/gm)}{SA \; (m^2/gm)}$,

where PV is pore volume (measured in cubic centimeters per
gram) and SA is surface area (measured in square meters per
gram).

15   Both nitrogen and mercury porosimetry may be used to
measure pore volume in xerogels, precipitated silicas and
dialytic silicas. Pore volume may be measured by the
nitrogen Brunauer-Emmett-Teller ("B-E-T") method described
in Brunauer et al., J. Am. Chem. Soc., Vol 60, p. 309

20   (1938). This method depends on the condensation of nitrogen
into the pores of activated silica and is useful for
measuring pores with diameters up to about 600A. If the
sample contains pores with diameters greater than about
600A, the pore size distribution, at least of the larger

25   pores, is determined by mercury porosimetry as described in
Ritter et al., Ind. Eng. Chem. Anal. Ed. 17,787 (1945).
This method is based on determining the pressure required to
force mercury into the pores of the sample. Mercury
porosimetry, which is useful from about 30 to about 10,000

30   A, may be used alone for measuring pore volumes in silicas
having pores with diameters both above and below 600A.
Alternatively, nitrogen porosimetry can be used in
conjunction with mercury porosimetry for these silicas. For
measurement of APDs below 600A, it may be desired to compare

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the results obtained by both methods. The calculated PV
volume is used in Equation (1).

    For determining pore volume of hydrogels, a different
procedure, which assumes a direct relationship between pore
5   volume and water content, is used. A sample of the hydrogel
is weighed into a container and all water is removed from
the sample by vacuum at low temperatures (i.e., about room
temperature). The sample is then heated to about 450 to
700°F to activate. After activation, the sample is
10   re-weighed to determine the weight of the silica on a dry
basis, and the pore volume is calculated by the equation:

$$(2) \qquad PV\ (cc/gm) = \frac{\%TV}{100 - \%TV},$$

15   where TV is total volatiles, determined by the wet and dry
weight differential. An alternative method of calculating
TV is to measure weight loss on ignition at 1750°F, (see
Equation (9) in Example II). The PV value calculated in
this manner is then used in Equation (1).

20   The surface area measurement in the APD equation is
measured by the nitrogen B-E-T surface area method,
described in the Brunauer et al., article, _supra_. The
surface area of all types of appropriately activated
amorphous silicas can be measured by this method. The
25   measured SA is used in Equation (1) with the measured PV to
calculate the APD of the silica.

    The purity of the amorphous silica used in this
invention is not believed to be critical in terms of the
adsorption of soaps and phospholipids. However, where the
30   finished products are intended to be food grade oils care
should be taken to ensure that the silica used does not
contain leachable impurities which could compromise the
desired purity of the product(s). It is preferred,
therefore, to use a substantially pure amorphous silica,
35   although minor amounts, i.e., less than about 10%, of other

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inorganic constituents may be present. For example, suitable silicas may comprise iron as Fe_2O_3, aluminum as Al_2O_3, titanium as TiO_2, calcium as CaO, sodium as Na_2O, zirconium as ZrO_2, and/or trace elements.

The examples which follow are given for illustrative purposes and are not meant to limit the invention described herein. The following abbreviations have been used throughout in describing the invention:

A	—	Angstrom(s)
APD	—	average pore diameter
B-E-T	—	Brunauer-Emmett-Teller
C	—	capacity
Ca	—	calcium
cc	—	cubic centimeter(s)
cm	—	centimeter
Cu	—	copper
°C	—	degrees Centigrade
db	—	dry basis
°F	—	degrees Fahrenheit
Fe	—	iron
gm	—	gram(s)
ICP	—	Inductively Coupled Plasma
m	—	meter
Mg	—	magnesium
min	—	minutes
ml	—	milliliter(s)
P	—	phosphorus
PL	—	phospholipids
ppm	—	parts per million (by weight)
PV	—	pore volume
%	—	percent
RH	—	relative humidity
rpm	—	revolutions per minute
S	—	soaps

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SA	–	surface area
sec	–	seconds
TV	–	total volatiles
wt	–	weight

EXAMPLE I

(Amorphous Silica Oil Samples)

The properties of the amorphous silica used in these examples are listed in Table II.

TABLE II

Silica Sample	Surface Area[1]	Pore Volume[2]	Av. Pore Diameter[3]	Total Volatiles[4]
Hydrogel[5]	911	1.8	80	64.5

[1]- B-E-T Surface Area (SA) measured as described above.
[2]- Pore Volume (PV) measured as described above using hydrogel method.
[3]- Average Pore Diameter (APD) calculated as described above.
[4]- Total volatiles, in weight percent (wt.%) on ignition at 1750°F.
[5]- The hydrogel was obtained from the Davison Chemical Division of W. R. Grace & Co.

The Oil Samples used in the following examples were prepared by combining Oil A (see Table III), a caustic refined soybean oil sampled after caustic treatment and primary centrifuge but before water wash, with either Oil Sample E or Oil Sample E' degummed soybean oils prepared as described below and not subjected to caustic treatment. Oil Sample E' was prepared in the same manner as Oil Sample E of Table III, for which analytical results are shown; insufficient quantities of Oil Sample E' precluded separate analysis, but it is assumed that the identically degummed oils were substantially identical. Oil Sample A contained large quantities of soaps (362 ppm) determined by measuring

alkalinity expressed as sodium oleate (ppm) by A.O.C.S. Recommended Practice Cc 17-79. The acid degummed oils, having not been contacted with caustic, contained no soap, but contained significant levels of phosphorus, as indicated by the values for Oil Sample E, which contained 22.0 ppm phosphorus, measured by inductively coupled plasma ("ICP") emission spectroscopy.

Oil Sample A was mixed in varying proportions (as indicated in Table III) with Oil Sample E or E' to prepare Oil Samples B, C and D, which are relatively constant for phosphorus and associated metal ions but which contain significantly different levels of soap. Oil Sample B contained 75% Oil Sample A and 25% Oil Sample E. Oil Sample C contained 50% Oil Sample A and 50% Oil Sample E'. Oil Sample D contained 25% Oil Sample A and 75% Oil Sample E'. Each Oil Sample was analyzed as described above for trace contaminants (P, Ca, Mg, Fe and Cu) and for soaps. The results are shown in Table III.

The acid degummed oils (Oil Samples E and E') were prepared by heating 500.0 gm oil, covered with foil and blanketed with nitrogen, in a 40°C water bath. Next, 500 ppm 85% phosphoric acid (0.25 gm) was added to the oil and stirred for twenty minutes while maintaining the nitrogen blanket. Ten milliliters of de-ionized water was added and mixed for one hour. The sample was centrifuged at 2300 rpm for thirty minutes. The top layer was the degummed oil used in the experiment (the bottom layer, comprising the gums, was discarded).

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TABLE III

Oil Sample	Trace Contaminants, ppm[1]					Soap, ppm[3]
	P	Ca	Mg	Fe[2]	Cu[2]	
A	13.4	0.93	1.03	0.02	0.02	362.0
B	19.4	2.08	1.92	0.00	0.02	180.0
C	20.8	3.04	2.46	0.06	0.01	70.0
D	23.7	3.84	3.01	0.07	0.02	30.0
E	22.9	4.27	3.17	0.11	0.03	0.0
E'	*	*	*	*	*	*

1- Trace contaminant levels (P, Ca, Mg, Fe, Cu) measured in parts per million by ICP emission spectroscopy.
2- Fe and Cu values reported were near the detection limits of this analytical technique.
3- Soap measured by A.O.C.S. Recommended Practice Cc 17-79.
*- Oil Sample E' was prepared from the same crude oil as Oil Sample E, and by identical acid degumming steps. Insufficient quantities of Oil Sample E' were available for analysis, but it is assumed that the values are comparable to those of Oil Sample E.

EXAMPLE II

(Treatment Of Oil Samples With Silica)

The Oil Samples prepared in Example I were treated with the amorphous silica described in Example I. For each test a 100.0 gm quantity of the Oil Sample (A, B, C, D, or E) was heated at 100°C, and the silica was added in the amount indicated in Table IV. The mixture was maintained at 100°C, while being stirred vigorously, for 0.5 hours. The silica was separated from the oil by filtration. The treated, filtered Oil Samples were analyzed for soap and trace contaminant levels by the methods described in Example I. The results, shown in Table IV, indicate that:

1. The amorphous silica adsorbent removed soaps and trace contaminants (phospholipids and associated metal ions) from the Oil Samples in a single operation.

2.   Soaps appeared to be preferentially adsorbed as compared to trace contaminants. In many cases there were no soaps found in the silica treated oil, while there were considerable trace contaminants remaining in the oil.

5   3.   The capacity of the silica adsorbent for phosphorus appeared to increase with increasing soap levels in the Oil Samples. For example, in Oil Sample A (362 ppm soap), a silica loading of only 0.15 wt.% was required to reduce the phosphorus level to well below 1.0 ppm, while in

10   Oil Samples C, D and E (70, 30 and 0 ppm soap, respectively) silica loadings of 0.6 wt.% were required to reduce phosphorus levels to below 1.0 ppm. The presence of soaps in the oil therefore made it possible to reduce phosphorus levels to below 1.0 ppm at a much lower silica usage than

15   was required in the absence of soaps.

The data obtained from Example II demonstrate that the capacity of amorphous silica for phospholipid and soap removal actually increases with increasing soap content of the starting oil until a maximum adsorbent capacity is

20   approached. The maximum adsorbent capacity of the silica hydrogel used under the conditions of Example II was approximately 55 wt.% soaps plus phospholipids.

The data in Table V were calculated from Table IV inorder to obtain values for the adsorption capacity of the

25   amorphous silica. Calculations were made as follows. The capacity of the amorphous silica for combined soaps and phospholipids (C_{S-PL}), expressed as a percent, can be defined as:

(3) $$C_{S-PL} = \frac{[\Delta S \text{ (ppm)} + \Delta PL \text{ (ppm)}]}{\text{Silica (db, wt.\%)}} \times 10^{-2}$$

30

where the change in concentrations of soaps and phospholipids in the oil (from before to after contact with the silica adsorbent) are defined as:

22.

(1) $\Delta S(ppm) = S(ppm)_{initial} - S(ppm)_{final}$

(5) $\Delta PL(ppm) = \Delta P(ppm) \times 30$

(6) $\Delta P(ppm) = P(ppm)_{initial} - P(ppm)_{final}$

(7) $Silica(db, wt.\%) = \dfrac{Silica(db, gm)}{Oil(gm)} \times 100$

where "Silica (db, gm)" is the weight in grams of the silica after ignition at 1750°F.

(8) $Silica(db, wt.\%) = Silica(as\ is, gm) \times \dfrac{100 - TV}{100}$

(9) $TV = 100 \times \left[\dfrac{Silica(as\ is, gm) - Silica(db, gm)}{Silica(as\ is, gm)}\right]$

The capacity of the amorphous silica for phospholipids alone (C_{PL}), expressed as a percent, can be defined as:

(10) $C_{PL} = \dfrac{PL(ppm)}{Silica(db, wt.\%)} \times 10^{-2}$

The calculated values for changes in phosphorus (P), phospholipids (PL) and soap (S), combined phospholipid and soap (S-PL) remaining in the oil, capacity for combined soap and phospholipid ($\%C_{S-PL}$) are given in Table V for each of the treated Oil Samples, along with starting phosphorus and soap values. The data from Table V were plotted in FIGURE 1 in the form of adsorption isotherms, with the wt.% phospholipids and soaps adsorbed on the silica (Δ S-PL) plotted on the ordinate versus the amount of soap and phospholipid remaining in the adsorbent-treated oil (Remaining S-PL) plotted on the abscissa. The data were plotted in this manner in order to correct for the phenomena typically observed for adsorption of increasing capacity (up to some plateau value as a result of saturation) with increasing adsorbate remaining in the treated material.

_23._

This phenomenon is predicted from equilibrium
considerations.

The data from Table V were also plotted in FIGURE 2 in
the form of adsorption isotherms, with the wt.%
5   phospholipids adsorbed on the silica (Δ PL) plotted in the
ordinate versus the amount of phosphorus remaining in the
adsorbent-treated oil (P) plotted on the abscissa. FIG. 2
shows data for adsorbent-treated Oil Samples with $\leq$30 ppm
residual soaps.

10   The data from Table V and Figures 1 and 2 indicate the
following:

1. The capacity of the silica for phospholipid and
soaps tends to increase with increasing levels of soap in
the starting oil.

15   2. Increasing soap content on the silica tends to
increase the phospholipid capacity of the silica when the
soap content in the treated oil has been significantly
reduced for example, in this case, about 30 ppm soap, as
demonstrated in Table V and Figure 2, for these Oil Samples
20   and this adsorbent.

The principles, preferred embodiments and modes of
operation of the present invention have been described in
the foregoing specification. The invention which is
intended to be protected herein, however, is not to be
25   construed as limited to the particular forms disclosed,
since these are to be regarded as illustrative rather than
restrictive. Variations and changes may be made by those
skilled in the art without departing from the spirit of the
invention.

Table IV
Trace Contaminant Levels ppm

Oil	Wt.% Silica	P	Ca	Mg	Fe	Cu	Soap, ppm
A	—	13.4	0.927	1.03	.019	.020	362.24
A	0.05	13.2	1.24	1.40	.0161	.0549	82.18
A	0.08	9.49	1.58	1.30	.0497	.0142	42.62
A	0.15	.013	.016	.021	.027	.014	0
A	0.30	.21	.021	.029	0	.006	0
A	0.6	.002	.045	.023	.128	.026	0
B	—	19.4	2.08	1.92	0	.0219	179.59
B	0.08	4.83	.643	.512	.0683	.148	30.44
B	0.15	1.70	.458	.431	.0805	.0258	0
B	0.3	.297	.160	.137	0	.0211	0
C	—	20.8	3.04	2.46	.063	.012	120.50
C	0.15	7.11	1.72	1.35	.070	.020	0
C	0.3	2.69	1.01	.799	0	.014	
C	0.6	.78	.518	.351	0	.010	0
D	—	23.7	3.84	3.01	.078	.015	30.00
D	0.15	11.1	3.18	2.51	.025	.012	0
D	0.3	7.72	2.63	2.00	.066	.015	0
D	0.6	.072	.396	.335	.407	.076	0
E	—	22.9	4.27	3.17	.110	.0306	0
E	0.15	12.1	3.63	2.87	.0713	.0447	0
E	0.3	6.77	2.59	1.99	.396	.0732	0
E	0.6	.319	.0847	.0532	0	.0164	0

25.

TABLE V

Oil	Wt% SiO$_2$	P (ppm)	S (ppm)	ΔP (ppm)	ΔPL (ppm)	ΔS (ppm)	ΔS-PL (ppm)	Remaining S-PL (ppm)	%C S&PL	%C PL
A	—	13.4	362	—	—	—	—	—	—	—
A	0.05	13.2	82	0.2	6	280	286	396	57.2	1.2
A	0.08	9.49	43	3.9	117	319	436	285	54.5	14.7
A	0.15	.013	0	13.4	402	362	764	0	50.9	26.8
A	0.3	.21	0	13.2	396	362	758	6	25.3	13.2
A	0.6	.002	0	13.4	402	362	764	0	12.7	6.7
B	—	19.4	180	—	—	—	—	—	—	—
B	0.08	4.83	30	14.6	437	150	587	145	73.4	54.6
B	0.15	1.7	0	17.7	531	180	711	51	47.4	35.4
B	0.3	.297	0	19.1	573	180	753	9	25.1	19.1
C	—	20.8	70	—	—	—	—	—	—	—
C	0.15	7.11	0	13.7	411	70	481	213	32.0	27.4
C	0.3	2.69	0	18.1	543	70	613	81	20.4	18.1
C	0.6	.78	0	20.0	601	70	671	23	11.2	10.0
D	—	23.7	30	—	—	—	—	—	—	—
D	0.15	11.1	0	12.6	378	30	408	333	27.2	25.2
D	0.3	7.72	0	16.0	479	30	509	232	17.0	16.0
D	0.6	.72	0	23.0	689	30	719	22	12.0	11.5
E	—	22.9	0	—	—	—	—	—	—	—
E	0.15	12.1	0	10.8	324	0	324	363	21.6	21.6
E	0.3	6.77	0	16.1	484	0	484	203	16.1	16.1
E	0.6	.319	0	22.6	677	0	677	10	11.3	11.3

WE CLAIM:

1.   A process for the removal of soaps and phospholipids (together with associated metal ions) from glyceride oil, characterized in that a caustic treated or caustic refined glyceride oil which comprises soaps and phospholipids is contacted with an adsorbent which comprises a suitable amorphous silica allowing said soaps and phospholipids to be adsorbed onto the amorphous silica and separating the adsorbent-treated oil from the adsorbent.

2.   The process of Claim 1 in which said caustic treated or caustic refined glyceride oil comprises at least about 5 parts per million soaps and at least 1 part per million phosphorus.

3.   The process of Claim 2 in which said caustic treated or caustic refined glyceride oil comprises at least 50 parts per million soaps.

4.   The process of Claims 1 to 3 in which said amorphous silica has an effective average pore diameter of greater than 60 Å.

5.   The process of Claim 4 in which at least 50% of the pore volume of said silica is contained in pores of at least 60 Å in diameter.

6.   The process of Claims 1 to 5 in which said amorphous silica is selected from the group consisting of silica gels, precipitated silicas, dialytic silicas, and fumed silicas.

7.   The process of Claims 1 to 6 in which said amorphous silica has a surface area of up to about 1200 m².

8.   The process of claims 1 to 7 in which said glyceride oil is contacted with said amorphous silica at a point in the refining process after caustic treatment or caustic refining so that said glyceride oil comprises at least 5 parts per million soaps.

9.   The process of claims 1 to 8 in which said caustic treated or caustic refined oil is contacted with amorphous silica at a silica usage of at least 0.1 weight percent.

10.   The process of claims 1 to 9 comprising the subsequent step of treating the silica-treated glyceride oil with bleaching earth.
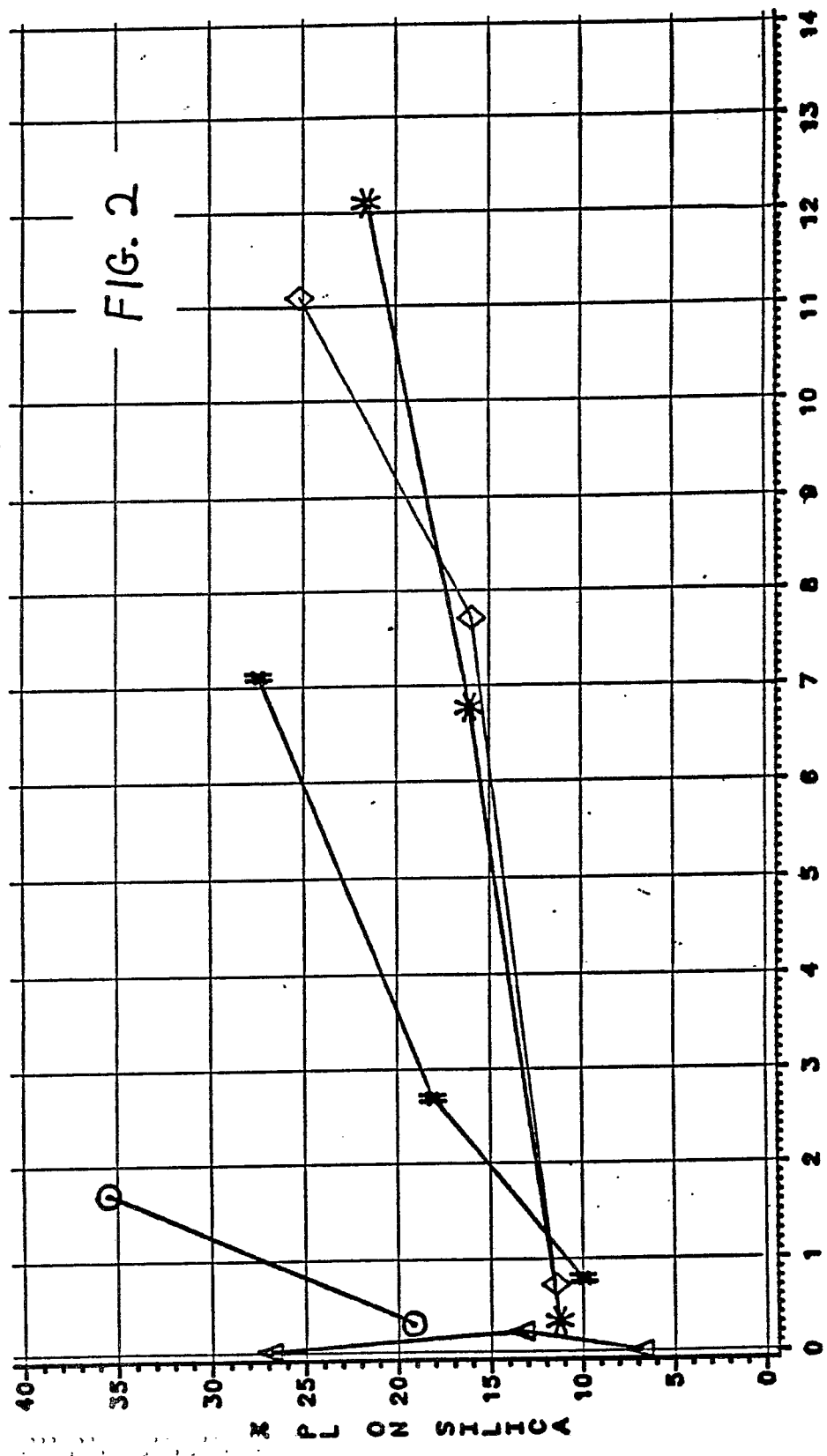
CAPACITY OF SILICA FOR PL & SOAP

CAPACITY FOR PL&S VS PPM PL&S REMAINING IN OIL
"S=" IN LABEL DESIGNATES STARTING SOAP VALUE

FIG. 1

LEGEND: ID **#*# S=0   6-6-6 S=180   ◇-◇-◇ S=30   4-4-4 S=362   #-#-# S=70
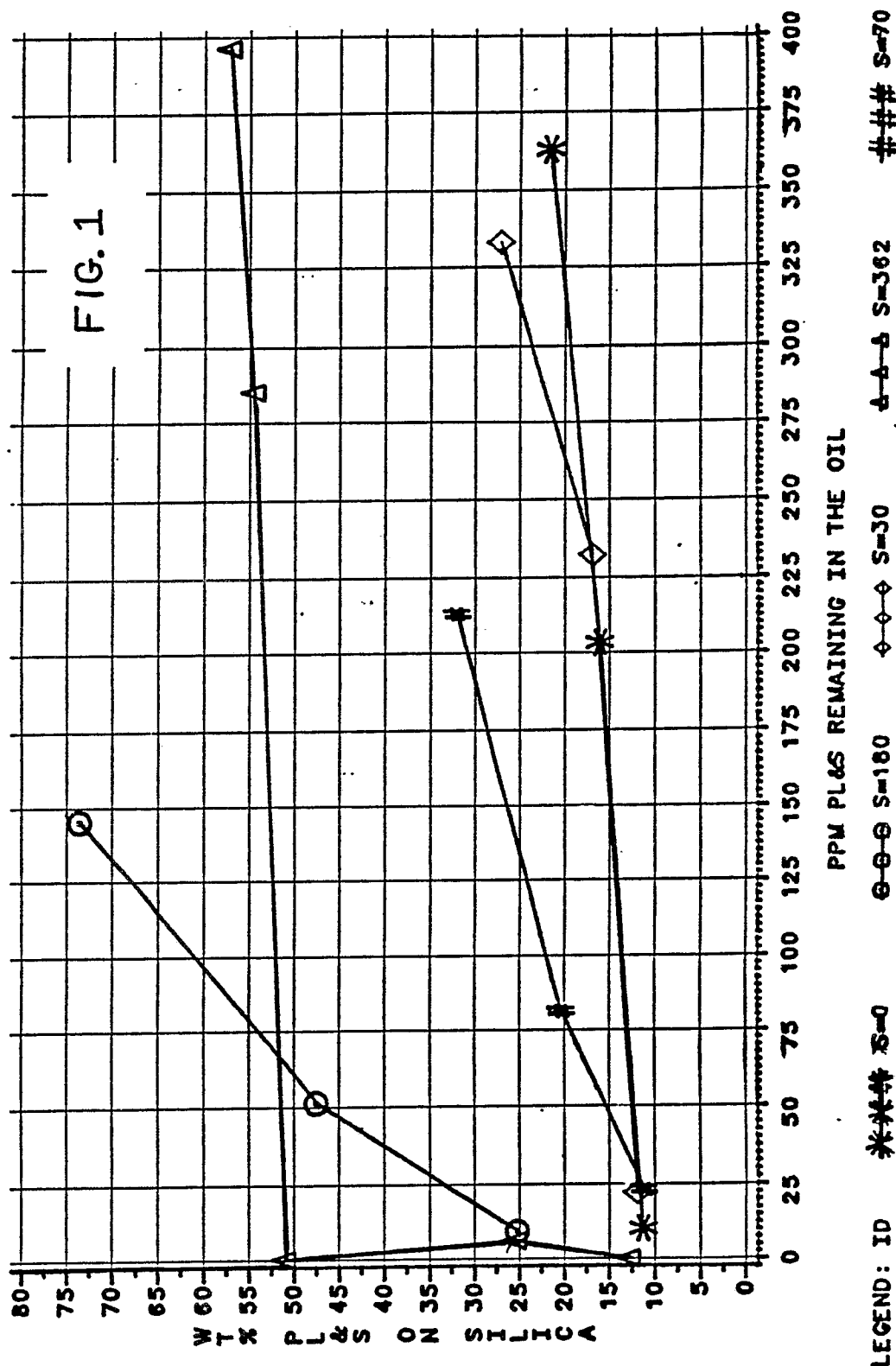
CAPACITY OF SILICA FOR PHOSPHOLIPID (PL)

CAPACITY FOR PL VS PPM P REMAINING IN THE OIL

"S=" IN LABEL DESIGNATES STARTING SOAP LEVEL IN THE OIL

PLOT FOR SAMPLES WITH LESS THAN OR EQUAL TO 30 PPM SOAP REMAINING

FIG. 2

PPM P REMAINING IN OIL

LEGEND: ID   ✳✳✳ S=0   ⊕⊕⊕ S=30   ◇◇◇ S=30   ⧄⧄⧄ S=362   ⧣⧣⧣ S=70

⊖⊖⊖ S=180

PL ON SILICA (vertical axis, values 0, 5, 10, 15, 20, 25, 30, 35, 40)

European Patent Office

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A- 599 595 (ANDERSON, CLAYTON & CO.) * Claims 1,3-5 *	1	C 11 B 3/10
P,X	EP-A-0 185 182 (GRACE) * Claims 1,2,4,5,9-11,13,21 *	1,2,4-7,10	
P,X	CHEMICAL ABSTRACTS, vol. 105, no. 23, December 1986, page 503, abstract no. 207837k, Columbus, Ohio, US; & SU-A-1 253 993 (CENTRAL-ASIAN SCIENTIFIC-RESEARCH etc.) 30-08-1986 * Abstract *	1,5,6,9	

TECHNICAL FIELDS
SEARCHED (Int. Cl.4)

C 11 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-09-1987	PEETERS J.C.