Effect of Concentration of Some Nickel Catalyst Poisons in Oils on the Course of Hydrogenation

BRONISLAW DROZDOWSKI and **MARIA ZAJAC,** Technical University of Gdańsk, Institute of Organic and Food Chemistry and Technology, Gdańsk, Poland

ABSTRACT AND SUMMARY

Hydrogenation has been carried out in a "dead-end" type reactor with various types of nickel catalyst and with automatic recording of hydrogen absorption. Oils with varying concentrations of sulfur and phsphorus compounds, fatty acids and their salts, as well as partly oxidized oils have been hydrogenated. The resulting kinetic curves are characteristic for each catalyst type and for each inhibitor. An increase in the poison concentration in the reaction system results in lengthening of the induction period apart from the decrease of the catalyst activity.

INTRODUCTION

The poisons for nickel catalyst are mainly present in the oil itself. Refining and bleaching the oil are of fundamental importance as the inhibitors of hydrogenation are present even after these processes. The following substances, among others, may have toxic effect on the catalyst: sulfur compounds, phosphorus compounds, free fatty acids, soaps, and oxidation products of the oil. The first three classes of compounds are natural components of vegetable oils, sulfur compounds being present mainly in the cruciferae oils. The remaining classes of compounds may appear during technological processing of oil.

Organic sulfur and phosphorus compounds present in oil are known to have a deleterious effect on nickel catalyst (1-12). Soaps and free fatty acids are regarded by some authors as toxic only at higher concentrations (1,13). No detailed data are available for the oxidation products. It may be generally stated that the publications on the poisoning of a nickel catalyst during the hydrogenation of oils are scarce.

EXPERIMENTAL PROCEDURES

Materials

Refined, bleached, and deodorized soybean oils were used as starting material for hydrogenation. Their characteristic data were as follows: free fatty acids (FFA) 0.1-0.2%, peroxide value (PV) 1.0-3.0 me O_2/kg, phospholipid (P) content 4-6 ppm, sodium soap content 2-3 ppm Na.

Three types of catalyst were used in the experiments: the 533 — unsupported, formate type, containing 10.3% Ni (Fat Factory, Gdańsk); RCH 55/5-FS — supported, containing 21.0% Ni (Hoechst); Nysel DM-3 — supported, containing 24.8% Ni (Harshaw).

Phospholipids were used as phosphorus compounds. They were isolated from soybean oil by hydration and chromatographic purification. Pure phospholipids (without glycolipids), dried over P_2O_5, were transferred to the hardened soybean oil. Thus the prepared sample (1.5% P) was introduced in the required quantity to the oil destined for hydrogenation.

As it appears from our earlier studies (9,10), allyl isothiocyanate (allyl-ITC) is particularly toxic. Therefore, this sulfur-containing compound was used in our studies, taking into account additionally, that it is the natural component of some oils. The product of Fluka AG, Chemische Fabrik Buchs SG was used for the preparation of standard oil solutions.

Free fatty acids were obtained by saponification of soybean oil followed by acidification of the soaps.

Sodium soaps were prepared by titration of an alcoholic solution of fatty acids with an alcoholic solution of NaOH. After the solvent was removed by evaporation under reduced pressure, the soaps were dried over P_2O_5 and transferred to the hardened oil. The sodium content in the sample was 1.2%.

In order to investigate the effect of oxidation products on hydrogenation, soybean oil was subjected to accelerated autoxidation by passing oxygen through it at a flow rate of 7.5 1/hr at 100 C.

Hydrogenation

Hydrogenations were carried out in a "dead-end" type reactor with automatic recording of hydrogen absorption. The constant conditions of hydrogenation were as follows: oil sample — 50 g; catalyst concentration — 0.1% Ni; temperature 160 ± 0.5 C; stirring rate — 2700 rpm; atmospheric pressure.

The catalyst was added after the process conditions became stable, and the oil was saturated with hydrogen. This moment was taken as the initial point of thre reaction.

The preselected inhibitors were added to the oil under hydrogenation. The following were the concentrations: allyl — ITC 6-57 ppm S; phospholipids 6-68 ppm P; sodium soaps 2-45 ppm Na; FFA 0.1-100%.

In order to determine the effect of oxidation degree on the reaction kinetics, oils having peroxide values in the range 1 to 107 me O_2/kg were hydrogenated.

The curves traced by the recorder express the volume of absorbed hydrogen (in cc) by 1 g of hydrogenated oil in relation to the reaction time. Therefore, they illustrate the reaction kinetics and we shall refer to them as kinetic curves.

RESULTS AND DISCUSSION

The course of hydrogenation in the presence of examined inhibitors is illustrated by the kinetic curves. A general examination of the kinetic curves shows that hydrogen absorption does not follow immediately after the introduction of a catalyst but only after a certain time called the "induction period."

Figures 1-3 represent the kinetic curves of soybean oil hydrogenation with the addition of allyl-ITC, phospholipids, and sodium soaps in the presence of three different catalysts. For the sake of clarity, the figures represent the kinetic curves corresponding only to some preselected inhibitor concentrations.

Figure 1 shows hydrogenation on the unsupported catalyst. The kinetic curve of soybean oil hydrogenation without inhibitor addition is traced with a thick solid line. The addition of 11 ppm of sulfur gives rise to a rather long induction period. However, about 12 min. after the introduction of the catalyst, rapid absorption of hydrogen is observed, and the slope of the curve is almost the same as for the reference oil. The induction period at the sulfur level of 34 ppm is as much as 30 min, and the slope of the curve is much less steep than that of the reference oil,
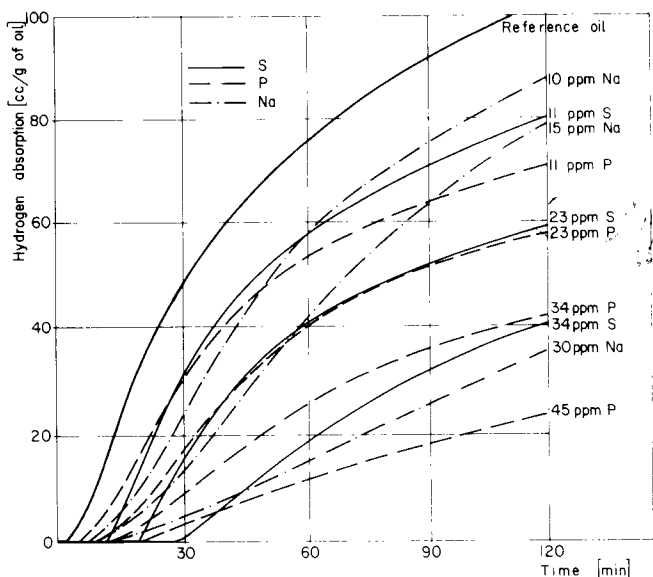
FIG. 1. Kinetic curves for the hydrogenation of soybean oil in the presence of sulfur, phosphorus, and sodium introduced to the system as allyl-ITC, phospholipids, and sodium soaps, respectively. Catalyst 533.
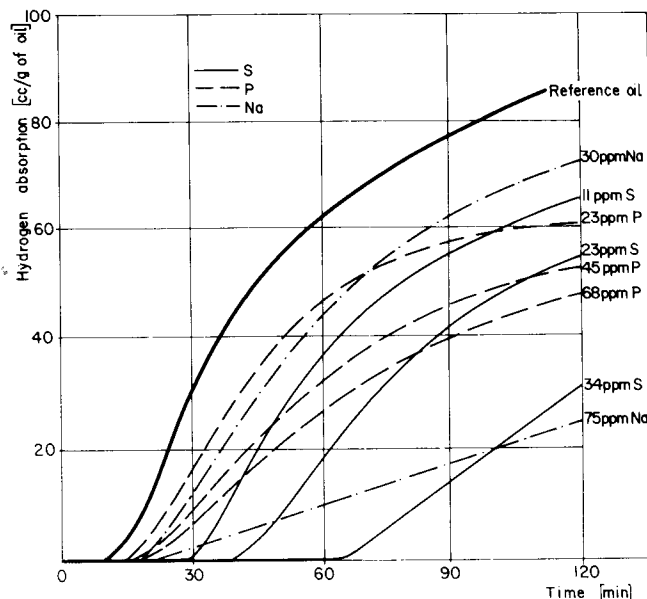

FIG. 3. Kinetic curves for the hydrogenation of soybean oil in the presence of sulfur, phosphorus, and sodium introduced to the system as allyl-ITC, phospholipids, and sodium soaps, respectively. Catalyst RCH 55/5-FS.
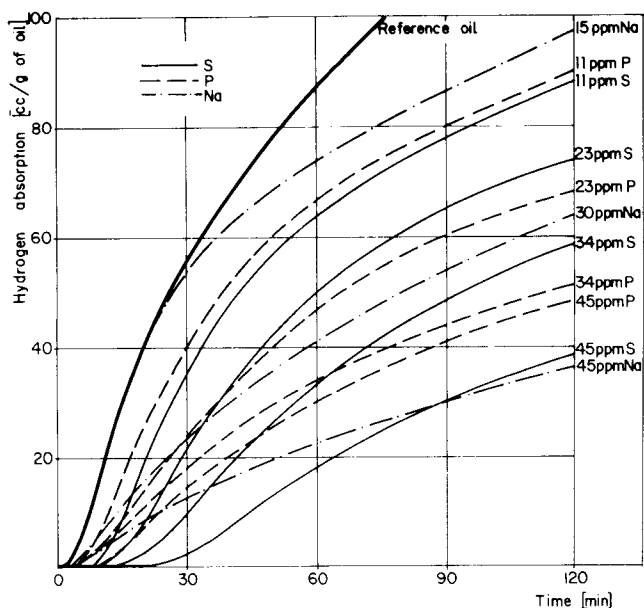

FIG. 2. Kinetic curves for the hydrogenation of soybean oil in the presence of sulfur, phosphorus, and sodium introduced to the system as allyl-ITC, phospholipids, and sodium soaps, respectively. Catalyst Nysel DM-3.

FIG. 4. Increase of the induction periods for different catalysts in relation to sulfur concentration introduced to the oil as allyl-ITC.

although the speed of the reaction is still prominent. A similar course of the curves is observed for phospholipids and soaps, but the induction periods are shorter.

Figure 2 represents the same relationship for Nysel DM-3 catalyst. The curves of Figure 3 are very characteristic. Allyl-ITC in the presence of RCH catalyst has a unique effect on the induction period. At the level of 11 ppm of sulfur in oil, it is as high as 30 min. However, after this period the hydrogenation course is almost the same as for the reference oil. This phenomenon, as apparent "depoisoning" of the catalyst, is very interesting but difficult to explain.

The comparison of all catalysts leads to the conclusion that allyl-ITC causes the greatest prolongation of the induction period, compared to phospholipids and soaps, and at the same time these periods change proportionally to
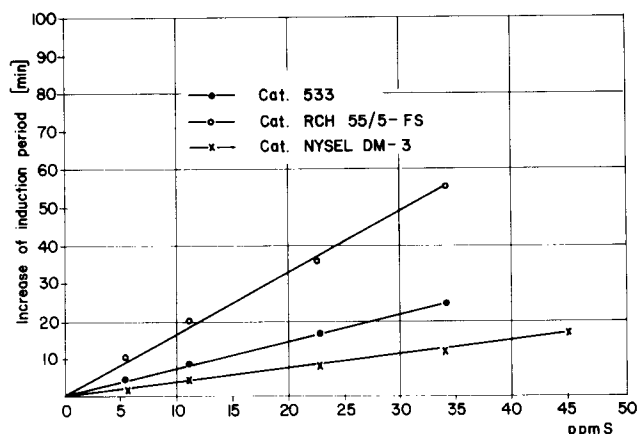
the increase of sulfur concentration in oil (Fig. 4). The diagram shows that the same increase of sulfur concentration in the oil causes a variable increase of the induction period for various catalysts; the greatest being for RCH 55/5-FS catalyst.

Expressing in turn induction periods caused by the presence of sulfur in the oil compared to the induction period of the initial oil, the greatest changes were noted for the 533 catalyst (Fig. 5).

During selective hydrogenation in industial conditions, is mainly the polyenoic acids that are reduced. Likewise in our studies the correlation between fatty acid composition changes and the kinetic curves shows that up to the level of hydrogen absorption of ca. 40 cc/g of oil it is mainly the polyenoic acids that undergo reduction. Having this in mind, we have considered the activity changes of the catalysts during the polyenoic acid hydrogenation, and the absorption level of 40 cc H_2/g was taken as the limiting value for all the hydrogenations. We have omitted the induction periods, and the activity changes were determined taking the activity during the initial oil hydrogenation as the reference.

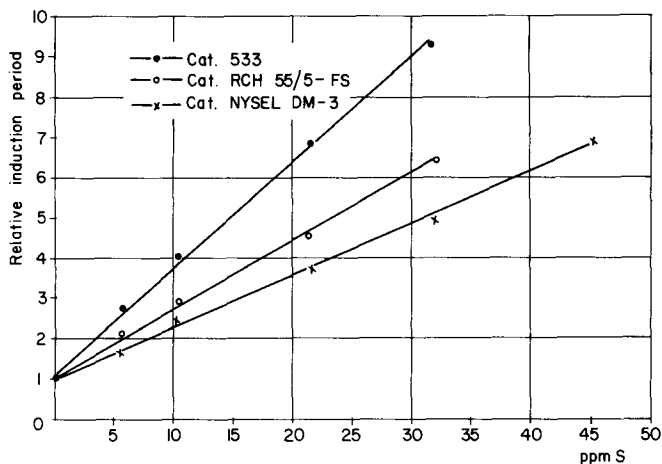The relative activity (A) of the catalysts was expressed as

FIG. 5. Relative change of the induction periods for different catalysts in relation to sulfur concentration introduced to the oil as allyl-ITC.
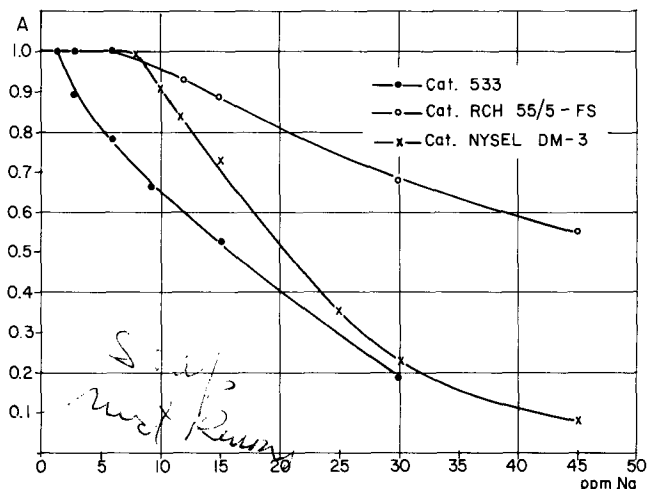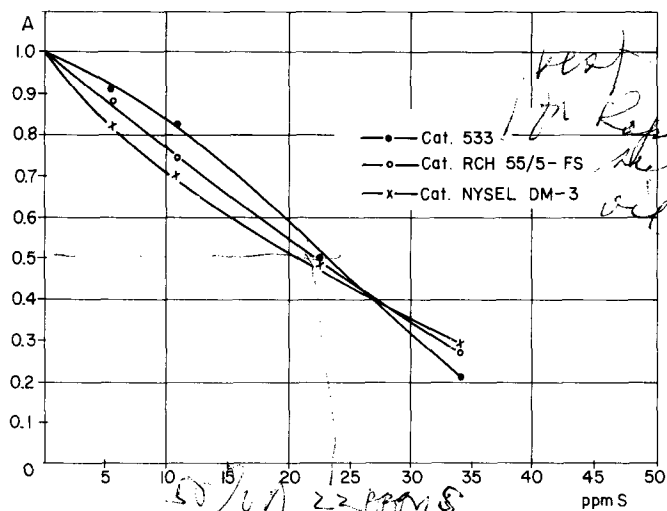

FIG. 6. Change in relative activity (A) for different catalysts in relation to sulfur concentration in the oil.

FIG. 7. Change in relative activity (A) for different catalysts in relation to phosphorus concentration in the oil.
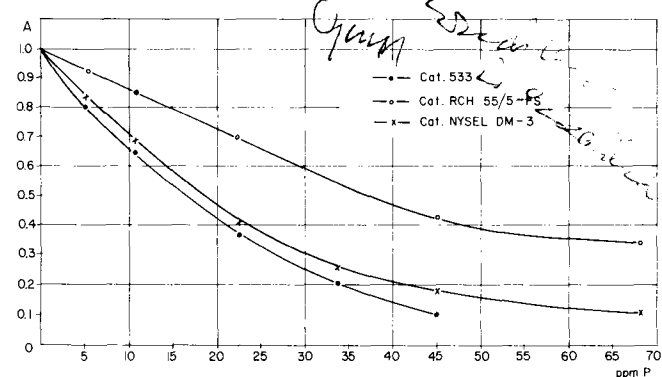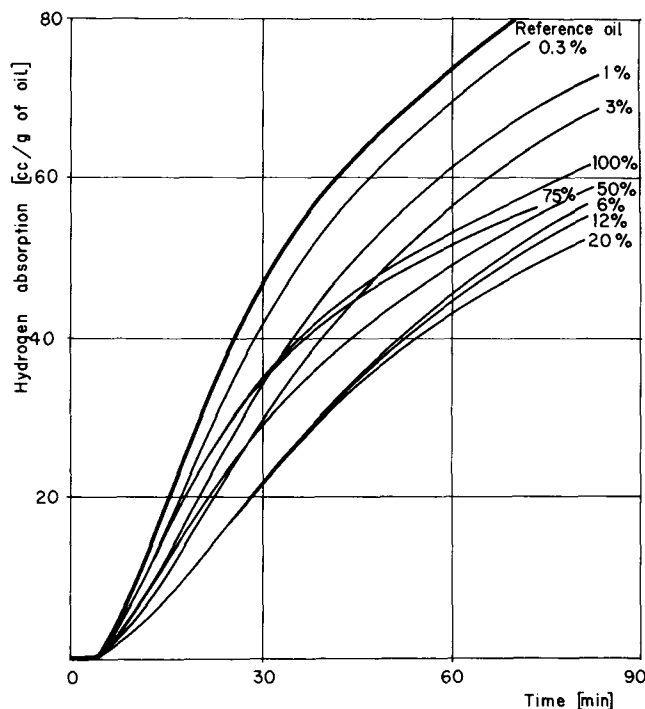

FIG. 8. Change in relative activity (A) for different catalysts in relation to sodium concentration in the oil.

FIG. 9. Kinetic curves for the hydrogenation of soybean oil in the presence of free fatty acids. Catalyst 533.

the ratio of the area under the curve obtained for the hydrogenation of the initial oil to the area corresponding to the reaction with the addition of inhibitors. The addition of allyl-ITC (Fig. 6) causes almost identical decreases of activity in all the catalysts.

Figure 7 shows that RCH 55/5-FS catalyst is most resistant to the presence of phospholipids in the oil, while the 533 catalyst is least resistant.

Considering the influence of soaps on nickel catalysts

(Fig. 8), we can say that they are nontoxic to the supported catalysts up to 8 ppm Na. For higher concentrations, Nysel DM-3 turns to be more sensitive to poisoning than RCH. The 533 unsupported catalyst is sensitive even below 8 ppm of Na. Above 8 ppm Na the speed of decrease of activity of Nysel DM-3 catalyst is greater than that of the others; although within the investigated range of concentration of sodium soaps, the greatest decrease of activity for the same amount of Na appeared for the 533 catalyst. It should be underlined that the above considerations do not include the influence of the induction periods on total reaction time.

Figures 9-11 represent the kinetic curves obtained by introducing FFA to the reaction system. The slope of the curves indicates that the increase of FFA in the oil up to 20% causes a constant decrease of the reaction rate when the hydrogenation is carried out in the presence of the 533 or Nysel DM-3 catalysts. In the case of RCH 55/5-FS catalyst, the same phenomenon is observed up to 6% of FFA in the oil. When these values are exceeded, the reaction rate starts to increase.
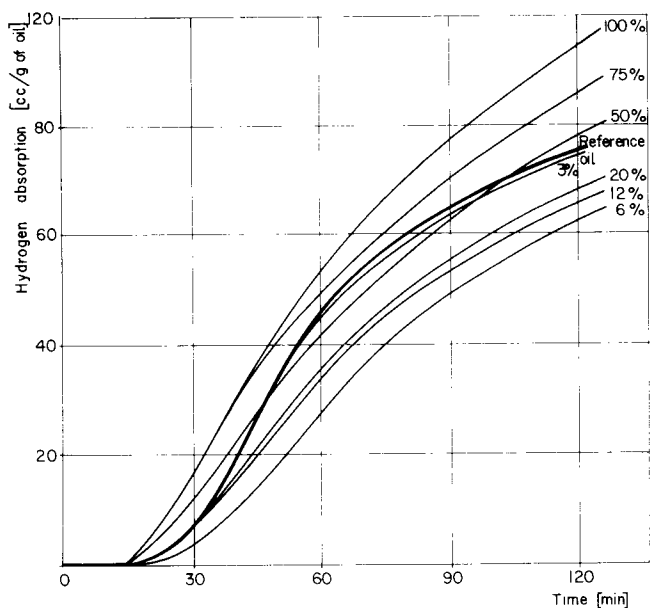
FIG. 10. Kinetic curves for the hydrogenation of soybean oil in the presence of free fatty acids. Catalyst RCH 55/5-FS.
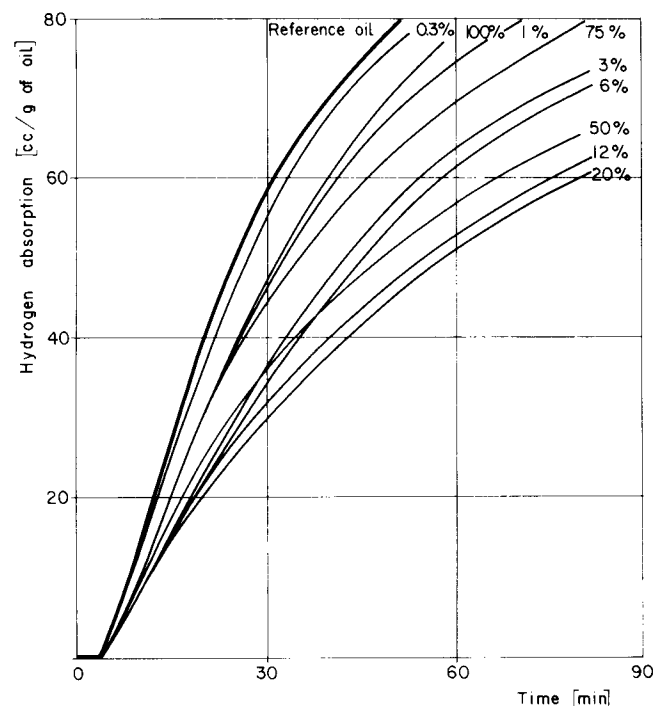

FIG. 11. Kinetic curves for the hydrogenation of soybean oil in the presence of free fatty acids. Catalyst Nysel DM-3.
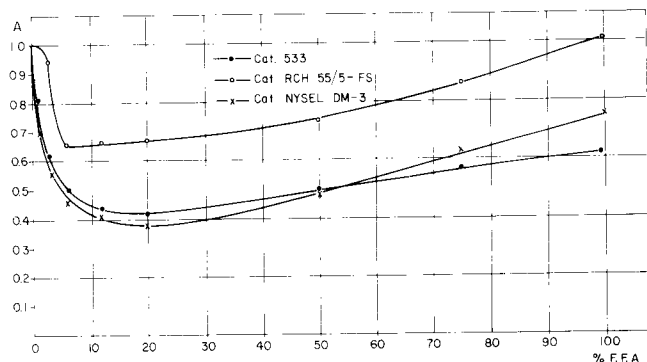

FIG. 12. Change in relative activity (A) for different catalysts in relation to free fatty acid concentration in the oil.
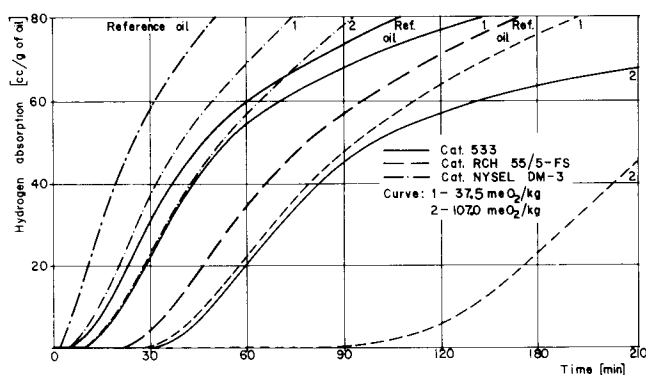

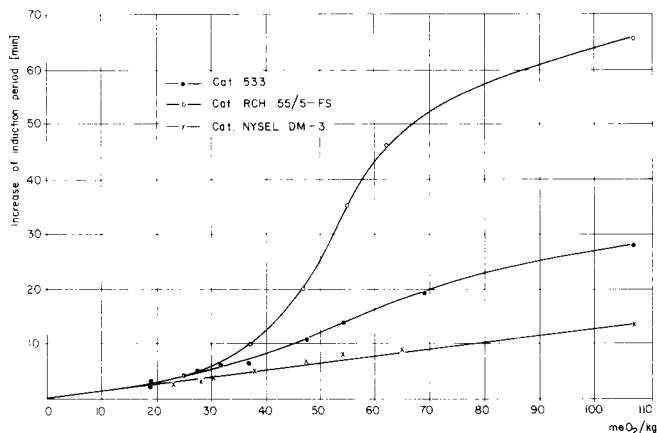FIG. 13. The course of kinetic curves for soybean oil hydrogenation in relation to oxidation degree.

FIG. 14. Increase of the induction periods for different catalysts in relation to oxidation degree of oil.

Unlike 533 and Nysel DM-3 catalysts, RCH catalyst hydrogenates free fatty acids faster than triglycerides (reference oil). For 533 and Nysel DM-3 a distinct drop of the reaction rate may be observed even below 1% FFA.

The change in relative activity (A) of the nickel catalysts are shown in Figure 12.

Neglecting the induction periods, we conclude on the basis of the kinetic curve slopes that RCH catalyst is the most resistant to the toxic action of the free fatty acids.

The initial loss of activity of the catalysts may be explained by the stronger adsorption of FFA than triglycerides on the catalysts, which results in the inaccessibility of some active centers for the latter. The increase in reaction rate at higher concentration of acids is a complex

problem that requires further investigation if it is to be explained.

The course of hydrogenation of oxidized oils is illustrated by the kinetic curves shown in Figure 13. The considerable increase of the induction period as a function of the oxidation degree of oil is similar to the increase caused by allyl-ITC. The shape of the curves (slope) suggests that the activity loss of the catalysts is relatively low. The variations of the induction periods (Fig. 14) indicate that their largest absolute increase is for RCH 55/5-FS, while the lowest one is for Nysel DM-3. Figure 15 respresents the induction periods due to the oxidation of oil in relation to the induction periods of the initial oil. The graphs suggest that the relative changes of the induction periods for the studied catalysts are close to one another.
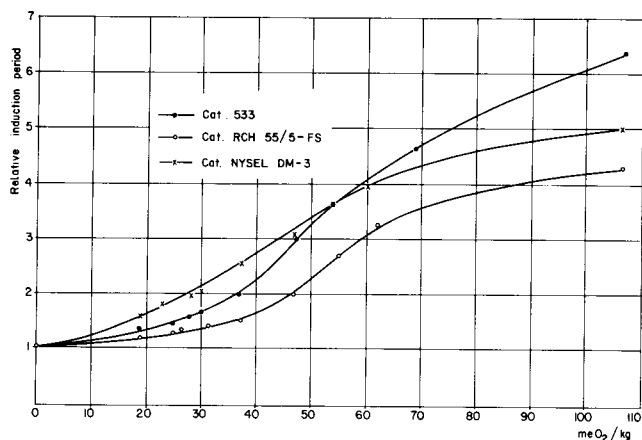
FIG. 15. Relative change of the induction periods for different catalysts in relation to oxidation degree of oil.

FIG. 16. Relative activity changes (A) for different catalysts in relation to oxidation degree of oil.

The relative activity (A) of catalysts during hydrogenation of partly oxidized oils (Fig. 16) remains the same up to about 30 me O_2 per 1 kg of oil. When this value is exceeded, loss of activity is observed. The lowest activity loss is noted for RCH 55/5-FS.

Other observations during the studies carried out indicate that the oils where the autoxidation process is spontaneous are hydrogenated much more slowly than are the oils subjected to accelerated autoxidation to the same peroxide value. Therefore, it is possible that the mechanism of oxidation is different for these cases given rise to different products which may have toxic effect on a catalyst.

Summing up, we can conclude that the character of the kinetic curves changes in the process of hydrogenation on the partly poisoned nickel catalysts depending on the type of catalyst and on the inhibitor introduced to the system.

The individual catalysts lose their activity to a different degree at the same level of inhibitor concentration. Moreover, we can observe that the relative degree of the activity loss of various catalysts changes with the concentration of an individual inhibitor.

The slopes of the kinetic curves suggest that RCH catalyst is the most resistant to the studied poisons. When one considers however, the generally employed kinetic methods of the catalyst activity evaluation based on the reaction progress in the standard conditions after 30 min, less frequently after 60 min., this catalyst is the least active and loses its activity to the greatest extent. Thus, the definition of activity requires a new interpretation which
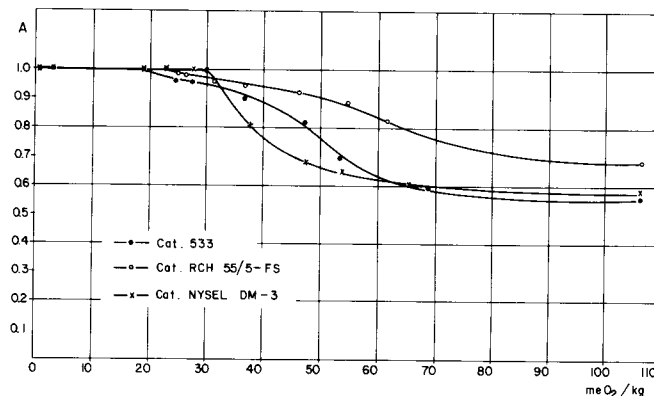
we intend to include in our next paper.

We would like to emphasize here that our studies confined to these specified catalysts were not aimed at the evaluation of their utility and quality.

REFERENCES

1. "Bailey's Industrial Oil and Fat Products," Edited by D. Swern, Interscience Publishers, New York, London, Sydney, 1964, p. 837.
2. Babuchowski, K., and A. Rutkowski, Seifen Oele Fette Wachse 95:27 (1969).
3. Stefanovic, S., and L.F. Albright, JAOCS 46:139 (1969).
4. Ottesen, I., Proceedings of the Sixth Scandinavian Symposium on Fats and Oils, Grena, Denmark, June, 1971, p. 129.
5. Notevarp, O. Ibid. p. 162.
6. Mørk, P.C., JAOCS 49:426 (1972).
7. Notevarp, O., R. Storleer, and A. Helgerud, Proceedings of the Seventh Scandinavian Symposium on Lipids, Røros, Norway, June, 1973, p. 169.
8. Norgard, D., Ibid. p. 188.
9. Drozdowski, B., H. Niewiadomski, and E. Szukalska, Przem. Chem. 52:556 (1973).
10. Drozdowski, B., E. Szukalska, and H. Niewiadomski, Tluszcze Jadalne 18:63 (1974).
11. Drozdowski, B., and M. Zajac, Ibid. 19:7 (1975).
12. Drozdowski, B., and M. Zajac, Ibid. 19:205 (1975).
13. Achaya, K.T., and D.S. Raju, J. Sci. Ind. Res. 29:68 (1970).

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