From Ellen Summers at the NCAA Library wrote on Divisional History:

Tex: To answer your question.

- In 1937 the NCAA established a College Committee. Its purpose was to provide a forum where matters of common interest of smaller colleges could be discussed and brought to the attention of the Association. However, there was no legislation to make the "College" an official classification. This was also the year when official statistics rankings began.
- In 1957, the Association established its first College Division
 Championships, however the "College Division" and "University Division"
 designations were not official until 1968, when the schools had to have
 their athletics program designated as one of the two classifications. Keep
 in mind, this classification was for athletic competition purposes only.
 There was no distinction between College Division and University
 Division when it came to bylaws and regulations. The 1973 restructuring
 was different in that it divided the member institutions both
 competitively and legislatively.
- When the smaller schools began to organize at the annual Convention to discuss their particular interests, it appears that led to the "unofficial" classification of small and large schools. However, at this time, I have not found any documentation that definitively speaks to that.